

# Open Research Online

---

The Open University's repository of research publications and other research outputs

## Models for Coordination and Reactivity at Silicon

### Thesis

How to cite:

Borbaruah, Moheswar (1991). Models for Coordination and Reactivity at Silicon. PhD thesis The Open University.

For guidance on citations see [FAQs](#).

© 1991 Moheswar Borbaruah



<https://creativecommons.org/licenses/by-nc-nd/4.0/>

Version: Version of Record

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.21954/ou.ro.00010150>

---

Copyright and Moral Rights for the articles on this site are retained by the individual authors and/or other copyright owners. For more information on Open Research Online's data [policy](#) on reuse of materials please consult the policies page.

---

[oro.open.ac.uk](http://oro.open.ac.uk)

DX95974

UNRESTRICTED

# MODELS FOR COORDINATION AND REACTIVITY AT SILICON

*A Thesis Submitted  
for  
The Degree of*

DOCTOR OF PHILOSOPHY IN CHEMISTRY

*To*

THE OPEN UNIVERSITY

MILTON KEYNES

1991

MOHESWAR BORBARUAH

Department of Chemistry  
The Open University  
Milton Keynes MK7 6AA  
UNITED KINGDOM

Date of submission : 21st October 1991

Date of award : 20th December 1991

ProQuest Number: DX95974

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest DX95974

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 – 1346

*Dedicated to my Mother*

## STATEMENT

*The work included in this thesis was carried out by the author during the period January 1989 to June 1991 in the Chemistry Department of the Open University under the supervision of Dr Alan R Bassindale.*

*Parts of the work have been presented/published in the abstract/journal listed below-*

- a) XXIIIth Organosilicon Symposium, Midland, USA, April 1990.*
- b) IXth International Symposium on Organosilicon Chemistry, Edinburgh, UK, July 1990.*
- c) XXIVth Organosilicon Symposium, El Paso, USA, April 1991.*
- d) J. Chem. Soc., Chem. Commun., 1499(1991) & 1501(1991)*

*Borbaruah*

*M Borbaruah*

*October 1991.*

## ACKNOWLEDGEMENTS

*I wish to record my gratitude to Dr Alan R Bassindale for his profound supervision and encouragement throughout the preparation of this work. My expression of gratitude would be incomplete were I not to mention that I also benefited in a multitude of ways by the exceptional kindness, unfailing help and generosity of Dr Bassindale.*

*I also wish to express my thanks to Dow Corning, Midland, USA, for their grant of financial assistance.*

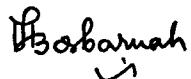
*I would like to express my appreciation to Mr Gordon Howell without whose cooperation the innumerable NMR recordings would have been impossible.*

*Members of the Chemistry Department deserve special compliments for their friendly attitude.*

*My wife's untiring moral support has been the greatest help of all.*

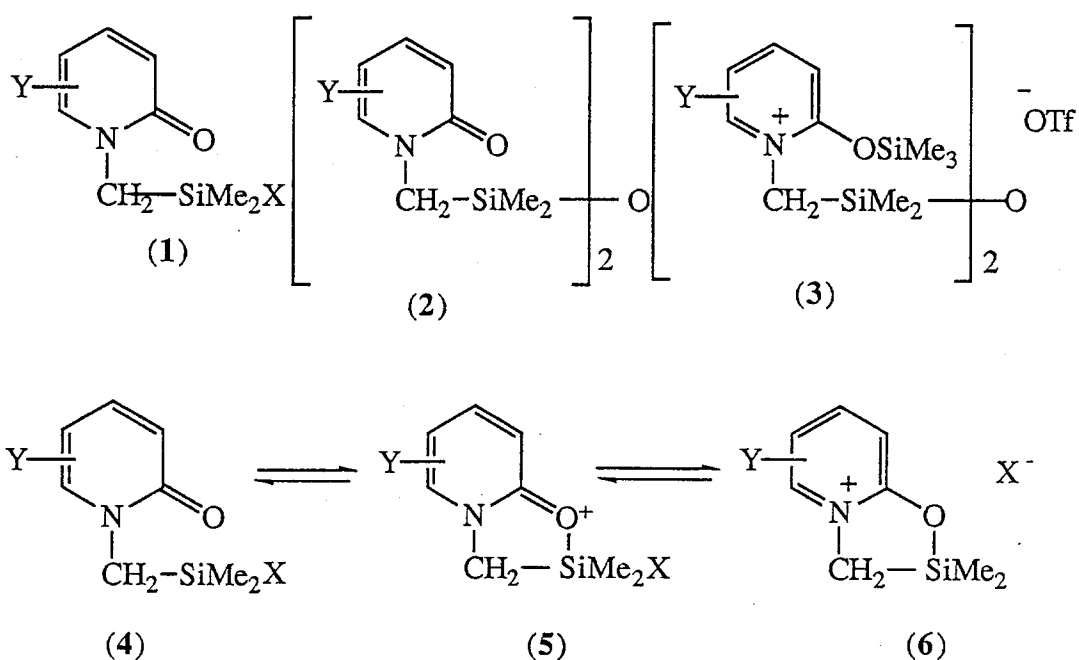
*Milton Keynes, UK*

*October 1991.*

  
(Moheswar Borbaruah)

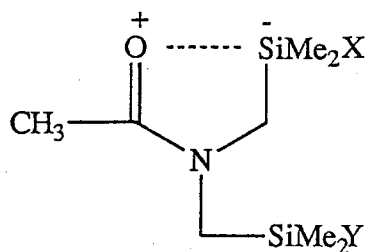
## ABSTRACT

We can now evaluate the effect of leaving group and nucleophile by examining, in solution, structures 'frozen' at particular points on the substitution profile. Twenty five compounds of the type, **1**, have been prepared and their NMR spectra compared with model compounds **2** and **3**. The position of **1** in the equilibrium **4**  $\rightleftharpoons$  **5**  $\rightleftharpoons$  **6** have



been inferred from  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra. For combinations of Y and X limiting structures **4**, **5** and **6** have been observed, as well as structures intermediate between **4** and **5**, and **5** and **6**. The leaving group ability falls  $\text{X}=\text{CF}_3\text{SO}_3 > \text{Br} > \text{Cl} > \text{F} > \text{OR}$ , and the equilibrium moves progressively to the right as Y becomes more electron donating.

We have also developed a model compound to investigate the relationship between coordination and reactivity at silicon. We used the compound **7** in which four and five coordinate silicon are present in the same molecule and their reactivity was compared. We used such compounds to study a) the ability of leaving groups to stabilize pentacoordination at silicon ( $X \neq Y$ ) and b) the relative reactivity to nucleophilic substitution of four and five coordinate silicon ( $X = Y$ ).

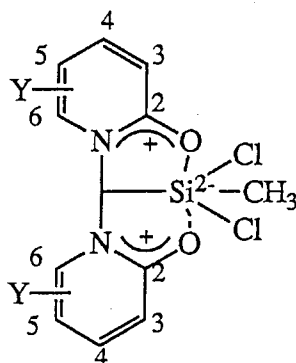


(7)

The reactions were studied by silicon-29 NMR. A nucleophile such as NMI or HMPA was added to the bis-silicon amide and the changes in the NMR spectra with varying amounts of nucleophile were recorded. It was found that five coordinate silyl chloride and bromide were more reactive than the four coordinate silyl chloride and bromide, but four coordinate silyl fluoride was found to be more reactive than the five coordinate silyl fluoride. When X and Y were different we found the ability to stabilize pentacoordinate silicon increases in the order  $\text{Br} > \text{Cl} > \text{F}$ .



Three new hexacoordinated silicon compounds of the type **8** have been prepared



(**8**) Y=H, 6-CH<sub>3</sub>, 3-OCH<sub>3</sub>

and their structures were determined by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR. Attempts were made to prepare suitable crystals for an X-ray structure but there were unsuccessful.

## CONTENTS

	Page
<u>Chapter 1</u> Introduction	
1.1 Introduction	2
1.2 Nucleophilic Displacement at Silicon	3
1.3 Complexes of Silicon Compounds	16
1.4 Reactivity of Hypervalent Silicon Compounds	25
 <u>Chapter 2</u>	
(Section A) An NMR Spectroscopic Method for Mapping Reaction in Solution.	
2.1A Introduction	45
2.2A Results and Discussion	46
(Section B) A Map of Nucleophilic Substitution at Silicon in Solution.	
2.1B Introduction	61
2.2B Results and Discussion	62
 <u>Chapter 3</u> Coordination and Reactivity at Silicon.	
3.1 Introduction	95
3.2 Results and Discussion	99
3.3 Conclusions and Summary	127

Chapter 4 Synthesis of Hexacoordinate Organosilylamides.

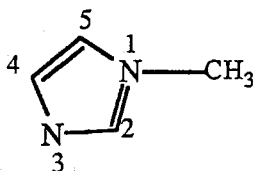
4.1	Introduction	142
4.2	Results and Discussion	144
	Experimental	153
	References	198

### List of abbreviations

acac	acetylacetone
OAc	acetate
R	alkyl or aryl
arom	aromatic
br	broad
NBS	N-bromosuccinimide
brs	broad singlet
C <sub>p</sub>	$\eta^5$ -cyclopentadienyl
d	doublet
DMSO	dimethylsulphoxide
DME	1,2-dimethoxyethane
Et	ethyl
eqv	equivalent
Et <sub>2</sub> O	ether
Fc	Ferrocene
HOMO	highest occupied molecular orbital
HMPA	hexamethylphosphoramide
Hz	Hertz
inv	inversion
i-Pr	isopropyl
J	coupling constant
LUMO	lowest occupied molecular orbital
M	metal

NMI

N-methylimidazole



m

multiplet

NR

no reaction

Nu

nucleophile

nBu

normal butane

nr

not recorded

Np

naphthyl

q

quartet

Ret

retention

Ref

reference

RT

room temperature

s

singlet

sbr

slightly broadened

t

triplet

OTf

trifluoromethanesulphonate (triflate,  $\text{CF}_3\text{SO}_3^-$ )

TMS

tetramethylsilane

THF

tetrahydrofuran

Vi

vinyl

# ***CHAPTER ONE***

## ***INTRODUCTION***

## 1.1 INTRODUCTION

Compared to carbon, silicon has a much smaller tendency to form compounds of coordination number less than four, but it has greater ability to increase its coordination sphere due to its vacant 3d orbitals. Hypervalent silicon compounds were first observed early in the nineteenth century, when Gay-Lussac and Davy reported<sup>1</sup> the formation of the adduct  $\text{SiF}_4 \cdot 2\text{NH}_3$ . A hexacoordinate cationic complex  $\text{Si}(\text{acac})_3^+ \text{HCl}_2^-$  was described by Dilthey<sup>2</sup> in 1903, and represented a new structural (i.e., chelated hexacoordinate) type for the element.

Organosilicon compounds with coordination number greater than four generally contain oxygen or nitrogen ligands, although recently the formation of the ion  $\text{C}_3\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}_2^-$  in the gas phase has been reported<sup>3</sup>. As the scope for additional coordination has been explored, interest in hypervalent silicon compounds has grown considerably during the last two decades. New structural types where inter- and intramolecular coordinations are favoured, have been developed and studies of permutational isomerisation in pentacoordinate species have been vigorously continued. Such studies are particularly relevant to the understanding of the stereospecificity generally observed in nucleophilic substitution at silicon, in which pentacoordinated intermediates are usually involved. The aim of this review is to focus upon the latest developments concerning nucleophilic displacement at silicon and to discuss the following topics.:

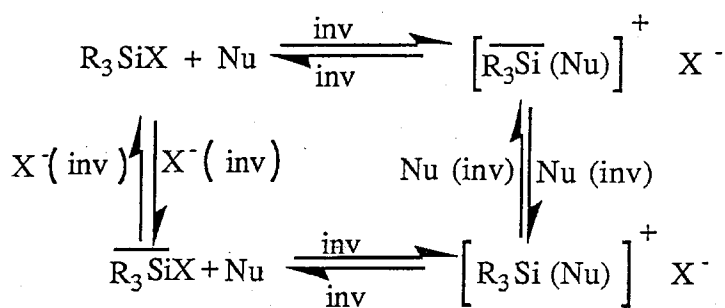
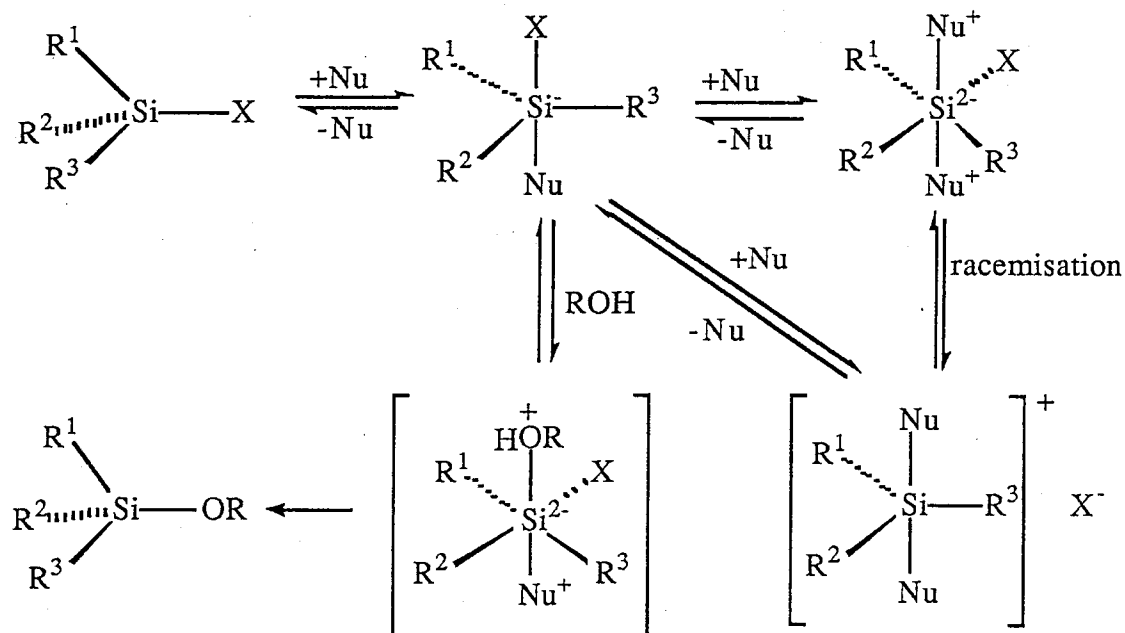
- 1.2) The factors affecting the outcome of nucleophilic substitution at silicon.
- 1.3) Complexes of silicon compounds.
- 1.4) Reactivity of hypervalent silicon compounds.

## 1.2 NUCLEOPHILIC DISPLACEMENT AT SILICON:

There has been much interest in investigation of the mechanism of nucleophilic substitution at silicon and it has been reviewed several times in recent years<sup>4,5</sup>. More recently Holmes has published a review on this topic<sup>6</sup>. Three mechanisms have been proposed for nucleophilically activated racemisation and solvolysis of halosilanes. One mechanism involves expansion of coordination at silicon with ultimately hexacoordinated intermediate species (Scheme 1.1)<sup>7</sup>. Racemisation can be accounted for by a reversible formation of a pentavalent silicon intermediate, followed by a second molecule of nucleophile to give either a pentavalent siliconium or hexavalent octahedral species. The second mechanism involves tetracoordinate ionic silicon species as intermediate with ionisation of Si-halogen bonds<sup>8</sup>. Recently, an alternative mechanism for nucleophilic assisted racemisation of halosilanes involving halide exchange has been suggested<sup>9</sup>. This has lead to an extension of the second mechanism as shown in Scheme 1.2. Inspite of many efforts in this field no clear distinction between the first two mechanisms can yet be made.

Nucleophilic substitution at carbon can take place either with inversion or racemisation of configuration at the carbon atom. But unlike carbon, nucleophilic substitution at silicon generally proceeds with high stereoselectivity, either retention or inversion of configuration at silicon but only rarely racemisation. Substitution at silicon can proceed either with retention or inversion of configuration and the stereochemical outcome depends upon the nature of the leaving group, the nucleophile, substrate structure etc. It is generally agreed that, opposite ( $180^\circ$  angle) attack of the nucleophile opposite to the leaving group produces an inversion, while an equatorial attack gives retention of configuration.





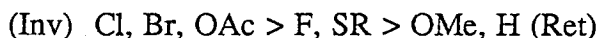
### Factors Controlling the Stereochemistry at Silicon:

- i) Structure of the silane: Although the structure of the substrate has almost no effect on the stereochemical outcome of substitution, the rate of substitution at silicon is susceptible to steric hindrance. Electronic effects of substituents are also

an important factor in determining the rate of the substitution. More highly hindered molecules react more slowly. A large decrease in the rate of substitution is observed<sup>10</sup> in the alkyl series- methyl, ethyl, iso-propyl, and tert-butyl. Release of electrons to the silicon atom by the alkyl groups assists in decreasing the rate of substitution. But the large reduction in reactivity observed here is too great to be attributed solely to the positive inductive effect of the alkyl substituents, and the steric effect is probably the dominant effect.

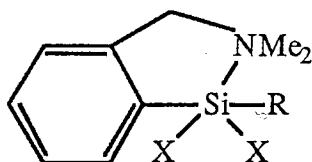
The stereochemical outcome of substitution is independent on the nature of the substrate for acyclic silanes. Replacement of a pentafluorophenyl group by phenyl group or by changing the substituents from moderate to bulkier groups did not alter the stereochemistry at silicon<sup>11</sup>. Sommer has shown<sup>11</sup> that cyclic silanes behave very differently both mechanistically and stereochemically from acyclic ones. More will be discussed in the section angle strain on silicon.

ii) Influence of the leaving group: When the leaving group at a chiral silicon centre is a good leaving group such as chloride or bromide, inversion of configuration is usually observed. Fluoride and thiol are bad leaving groups. Cleavage of Si-F or Si-SR bonds can give either retention or inversion depending upon the nature of the nucleophile entering into the displacement process. Si-H bond cleavage occurs mainly with retention of configuration, except with  $\text{Ph}_2\text{CHLi}$  where inversion of configuration is observed<sup>12</sup>. The Si-OR bond is displaced mainly with retention by Grignard and organolithium reagents<sup>13</sup>, except for some charge delocalised reagents e.g.,  $\text{PhCH}_2\text{Li}$ ,  $\text{Ph}_2\text{CHLi}$ . Corriu<sup>7a,13</sup> has observed that the tendency of halosilanes to undergo racemisation and the preference for inversion over retention of stereochemistry upon nucleophilic attack at silicon both follow the same trend as that of the relative ability of the leaving group to be displaced, and the order is-

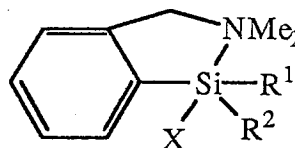


The attempted correlation of the stereochemistry of nucleophilic substitution at silicon with the  $pK_a$  of the conjugate acid of the leaving group or electronegativity or bond polarisability ( $I > Br > Cl$ ;  $SH, Br > Cl$ ;  $OH, OR > H > F$ )<sup>14</sup> has not been found to be very satisfactory. On the basis of  $pK_a$ , the SR is a very bad leaving group<sup>11</sup> (the corresponding conjugate acid, RSH, has a  $pK_a > 10$ ), so it should react with retention of configuration, but inversion is often observed<sup>15,16</sup>. Fluoro group ( $HF$ ,  $pK_a \approx 3.5-4$ )<sup>11</sup> should be a good leaving group and undergo inversion, but retention is often observed<sup>17,18</sup>.

Corriu has proposed<sup>13</sup> that electronegativity is not the controlling factor in determining the stability of extracoordinate silicon complexes, but depends upon the tendency of the Si-X bond to be stretched under the influence of an incoming nucleophile. The NMR studies on the compounds  $o-(Me_2NCH_2)C_6H_4SiX_2R$  (1.1) and  $o-(Me_2NCH_2)C_6H_4SiXR^1R^2$  (1.2) system indicate the expansion of

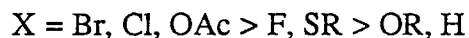


(1.1)

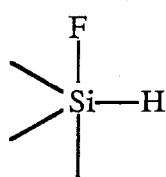


(1.2)

coordination at silicon by an intramolecular Si-N bond. He assessed the relative ease of pentacoordination at silicon which can be summarised as follows<sup>19</sup>, and which is the same order as for ease of inversion and racemisation.

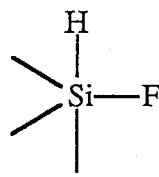


The low temperature  $^{19}\text{F}$  NMR studies on bifunctional organosilanes  $o\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{SiXFR}$  led Corriu<sup>20</sup> to define a scale of relative apicophilicity of various substituents X, bonded to pentacoordinate silicon atom. Apicophilicity can be defined as the change in energy when an apical and an equatorial substituent exchange positions in a trigonal bipyramid<sup>6</sup>. For example, the isomer energy difference  $E_B - E_A$  is the apicophilicity of fluorine relative to hydrogen,  $A(\text{F}_\text{H})$ .



(A)

(1.3)



(B)

(1.4)

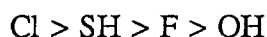
The ab initio molecular orbital calculations gave a positive value for the expression where structure 1.3 with the fluorine axial is more stable than 1.4.

The apical and equatorial fluorine can be distinguished because of their different  $^{19}\text{F}$  nmr chemical shifts. The shifting of fluorine-19 chemical shift to lower field at low temperature, indicates that the fluorine is apical or shifts to higher field show that the fluorine is equatorial. The fluorine atom occupies the apical position when  $X=\text{H, OR or NR}_2$  and  $\text{R}=\text{Me}$  but equatorial for  $X=\text{Cl}$ . Corriu<sup>20</sup> observed the following relative orders of apicophilicity for groups X bonded to the pentacoordinate silicon atom versus the apicophilicity of F.



The above sequence shows that chlorine is more apicophilic than fluorine although the latter is more electronegative. This may explain the stereochemical behaviour of 1-NpFcSi(Cl)F; only chlorine is displaced by carbon nucleophiles and inversion is the predominant stereochemistry<sup>21</sup>. In 1-NpFcSi(F)OR, only the fluorine is displaced and inversion is usually observed<sup>22,23</sup>. The group displaced in the substitution in the above mentioned cases is found to be in the apical position.

The apicophilicities for the series  $H_3SiXH$ , where H represents the nucleophile and X the various leaving groups, both occupying apical positions of a trigonal bipyramidal have been calculated theoretically by Deiters and Holmes<sup>24</sup>. They found that the apicophilicities lie in the order-

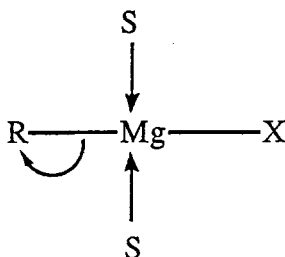


The order is found to be similar to that observed experimentally by Corriu<sup>20</sup>.

iii) Influence of the nucleophile: The stereochemistry at silicon is affected by the nature of the attacking nucleophile. The percentage of retention or inversion is dependent upon the structure of the anion, the cation and the solvent.

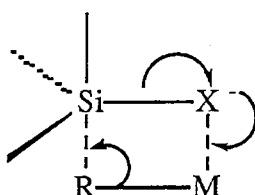
Corriu<sup>7a,13</sup> observed that hard nucleophiles give retention whereas soft nucleophiles give inversion of configuration for a particular leaving group. A hard nucleophile is a species which contain localised negative charge e.g.,  $R-Li^+$ . They prefer equatorial attack on silicon giving retention of configuration. On the other hand, a soft nucleophile is a species which has delocalised negative charge e.g.,  $PhCH_2-Li^+$  and prefer axial attack on silicon giving inversion. The stereochemistry at silicon can be altered by changing the metal cation or by altering the properties

of the solvent. Organolithium reagents show a general shift towards retention compared to Grignard reagents. The C-Mg bond of a Grignard reagent is moderately covalent compared to the C-Li bond of organolithium reagents and acts as a soft nucleophile and hence inversion is the predominant stereochemistry during substitution<sup>7a</sup>. By increasing the solvating power of the solvent, the stereochemistry at silicon can also be modified from inversion to retention for a particular nucleophile. Grignard reagents act as a hard nucleophile in nucleophilic solvents (e.g., THF, DME) due to coordination between solvent and the magnesium atom (Scheme 1.3) and reacts with retention.



Scheme 1.3 Coordination of solvent with Grignard reagent

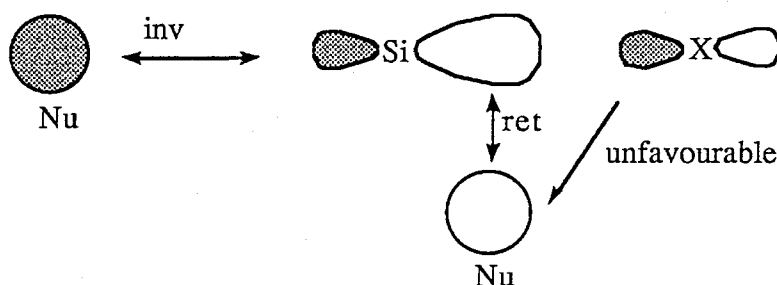
According to Sommer<sup>11</sup>, a quasicyclic  $S_Ni$ -Si transition state (Scheme 1.4) is responsible for the retention of configuration at silicon. The  $S_Ni$ -Si mechanism involves the electrophilic assistance to the leaving group by the  $M^+$  counterion.



Scheme 1.4  $S_Ni$ -Si mechanism

The factors which tend to increase the solvation of  $M^+$  should decrease the proportion of retention. These results are the complete opposite of those observed by Corriu<sup>25-27</sup>. Corriu therefore does not support the  $S_Ni$ -Si mechanism and favours the Molecular Orbital approach described below.

Anh and Minot<sup>28</sup> used a frontier orbital approach to rationalise the stereochemistry at silicon. Although the arguments are complex, they assumed that the major interaction during a reaction is that between the HOMO (Highest Occupied Molecular Orbital) of the nucleophile and LUMO (Lowest Unoccupied Molecular Orbital) of the tetracoordinated silicon species. As shown in Scheme 1.5. The front side attack leads to retention. When unfavourable, out-of-phase overlap between the nucleophile and the orbitals of the leaving group

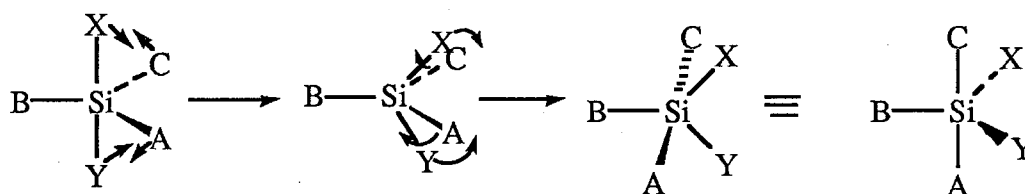


Scheme 1.5 Structure of the substrate LUMO,  $\sigma^*_{Si-X}$

predominates, nucleophilic attack occurs at the rear side of the molecule, opposite to the leaving group leading to inversion. Retention or inversion is the result of inphase and out-of-phase orbital overlap respectively between the nucleophile and the LUMO of the substrate. The nature of the nucleophile and the electronegativity of the leaving group have dramatic effect on the size of the HOMO and LUMO orbitals respectively. The s character at silicon atom increases with the

increase of electronegativity of the leaving group, leading to a bigger lobe between silicon and the leaving group and hence favours retention of configuration. It is observed that the retention is more favourable for fluorine relative to chlorine as leaving group. Hard nucleophiles, with contracted valence orbitals favours front side attack leading to retention of configuration. Rear side attack is enhanced with a soft nucleophile with diffuse valence orbitals and the out-of-phase orbital overlap dominates leading to inversion of configuration. Although the Anh and Minot approach gives a qualitatively rational explanation for most of the stereochemical data at silicon, the theory does not propose a role for pseudorotation.

The predominant stereochemistry for pentavalent silicon is trigonal bipyramidal. An interesting feature of trigonal bipyramidal molecule is the possibility of internal exchange or pseudorotation of their ligands. The process of pseudorotation was first described by Berry<sup>29</sup> and is shown in Scheme 1.6. The process involves the

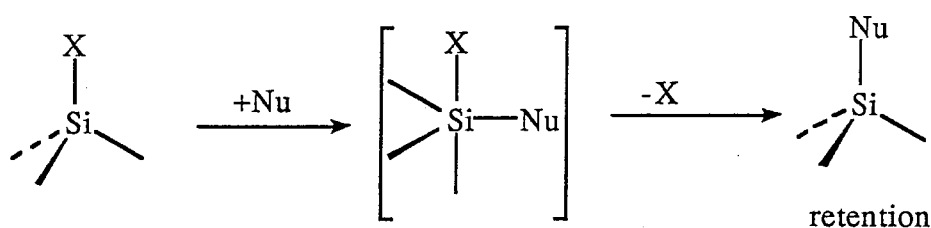


Scheme 1.6

exchange of axial ligands, X and Y with two of the equatorial ligands A and C, keeping the substituent B, called the pivot ligand unchanged. During pseudorotation, X and Y which are originally equatorial become axial. Similarly, ligands A and C are changed from equatorial to apical.



Holmes *et al*<sup>30</sup> have recently published X-ray crystallographic data of pentavalent silicon complexes, with geometries ranging from trigonal bipyramidal to square pyramidal which provides further evidence in support of Berry's pseudorotation. The pseudorotation process is not entirely ruled out by Corriu, but he suggested<sup>7</sup> an alternative mechanism which does not require a pseudorotation step as shown in Scheme 1.7. Equatorial attack by nucleophile is assumed in a tetrahedral edge between a ligand and the leaving group which results a five coordinated trigonal

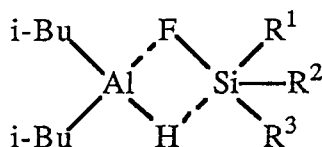


Scheme 1.7

bipyramidal intermediate. Axial departure of the leaving group in the process results in retention of configuration. Holmes<sup>24</sup> disagrees with this mechanism as *ab initio* calculations show it to be a very high energy process.

iv) Effects of solvent: It has been discussed earlier that by altering the properties of the solvent, the nature of the nucleophile can be altered. For example, Grignard reagents act as soft nucleophile in ether but as a hard one in THF or DME.

Alanes,  $\text{AlH}_n\text{Y}_{3-n}$  increase the extent of inversion at silicon as the basicity of the solvent increases.  $(i\text{-Bu})_2\text{AlH}$  substitutes all  $\text{Si-X}$  groups ( $\text{X}=\text{F}, \text{Cl}, \text{SR}, \text{OR}$ ) with retention of configuration in hexane<sup>30</sup>. Sommer<sup>11</sup> suggests that this is a result of a very strong electrophilic centre and a weaker nucleophilic centre with electrophilic assistance as shown in Scheme 1.8



Scheme 1.8

The percentage of inversion increases with the basicity of the solvent (hexane < Et<sub>2</sub>O < THF). It is argued that the Al-H bond of alanes is slightly polarised and hence acts as a hard nucleophile and gives retention. In the presence of a basic solvent, the coordination of the solvent at the aluminium atom delocalises the negative charge on hydrogen as shown in Figure 1.1 leading to inversion of configuration.

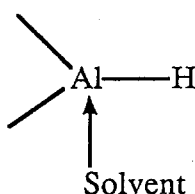
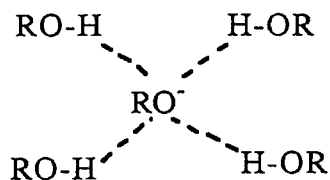


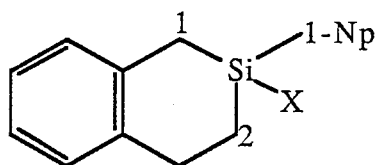
Figure 1.1 Coordination of solvent with alanes.

Corriu *et al*<sup>7a,13</sup> have found that the stereochemistry at silicon changes from retention to inversion when the alcohol content of the medium is increased. They argued the above observations in terms of electronic factors. They found that the nucleophiles RO-M<sup>+</sup> act as a hard nucleophiles in benzene and react with retention. When the alcohol content is increased, the charge is dispersed by strong hydrogen bonding interactions as shown in Scheme 1.9 and such dispersal of negative charge produces a softer species which reacts predominantly with inversion.



Scheme 1.9

v) Effects of angle strain at silicon: Angle strain at silicon has a dramatic effect on the stereochemistry of substitution at silicon. Increased angle strain at silicon changes the stereochemistry towards retention for exocyclic leaving groups except in compounds **1.5a** and **1.5b** which gives complete retention instead of inversion when treated with alkyl lithiums and alkyl Grignard reagents respectively<sup>32,33</sup>.



**1.5(a)** X=Cl

(b) X=F

The change of stereochemistry from inversion to retention with change of angle strain at silicon can be summarised as follows-

Inv			Ret
109°	105°	93-96°	90°
acyclic silanes	six-membered ring	five-membered ring	four-membered ring

Increased angle strain at silicon changes the stereochemistry toward inversion for endocyclic leaving groups<sup>34,35</sup>.

A possible interpretation generally invoked in phosphorus chemistry assumes that the four- or five membered rings are unable to occupy the diequatorial position of a trigonal bipyramidal intermediate and must occupy the apical-equatorial position<sup>36</sup>. The nucleophile attacks at 90° to the leaving group and hence leads to retention of configuration (Figure 1.2).

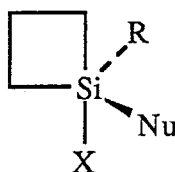


Figure 1.2

Anh and Minot<sup>28</sup> have argued that the stereochemistry at silicon can be explained in terms of change of hybridisation around the tetracoordinated silicon atom. If the angle is smaller than the tetrahedral value, the four hybrid atomic orbitals of silicon are no longer equivalent. The two used for making Si-C-1 and Si-C-2 (Scheme 1.10) bonds have less s character than the two remaining atomic orbitals (Si-R and Si-X). They have shown<sup>28</sup> that, an increase of s character implies an



Scheme 1.10

easier front side attack at silicon and therefore greater ratio of retention. Therefore, if the silicon atom is in a strained ring with exocyclic leaving group, the percentage of retention will increase, whereas, for endocyclic leaving group (Scheme 1.10) inversion of configuration will be favoured.

### 1.3 COMPLEXES OF SILICON COMPOUNDS:

Silicon has greater ability to form extracoordinated compounds than carbon. A large number of penta<sup>37-47</sup> and hexacoordinate<sup>48-52</sup> complexes of silicon are known compared to few proposed in carbon chemistry<sup>53</sup> and few a examples of hypervalent silicon compounds are shown in Figure 1.3. Hypervalent silicon

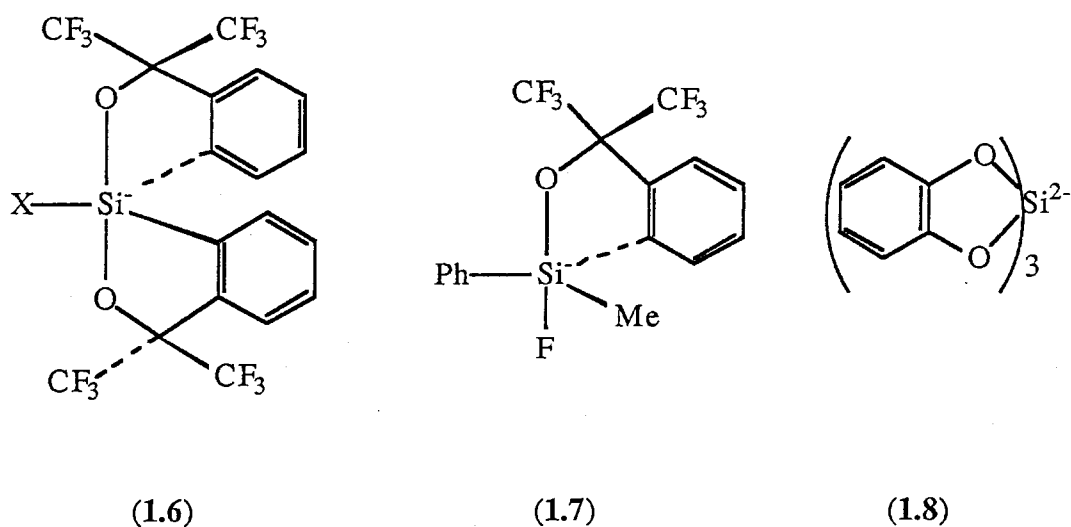


Figure 1.3

compounds generally contain halogen, nitrogen or oxygen ligands around the silicon. The predominant stereochemistry for five coordinate silicon is trigonal bipyramidal. But a number of hypervalent silicon compounds are known where the

presence of an intramolecular coordinating ligand modifies the geometry around the silicon atom from trigonal bipyramidal to square pyramidal<sup>30</sup>. Examples of a few intramolecular complexes are shown in Figure 1.4

Corriu *et al*<sup>40</sup> have used the induced diastereotopicity in **1.10** to study the dynamic behaviour by NMR spectroscopy. They observed two different dynamic processes, one with activation energy  $\Delta G^\ddagger$ , 9.4 kcal/mol and the other with  $\Delta G^\ddagger$ , 11.8 kcal/mol due to pseudorotation at silicon and breaking of the Si-N bond respectively. Klebe and Hensen<sup>54</sup> studied the dynamics of compound **1.12** by <sup>19</sup>F NMR and stated that the energy barrier for fluorine equilibration of 7.5 kcal/mol was best accounted for

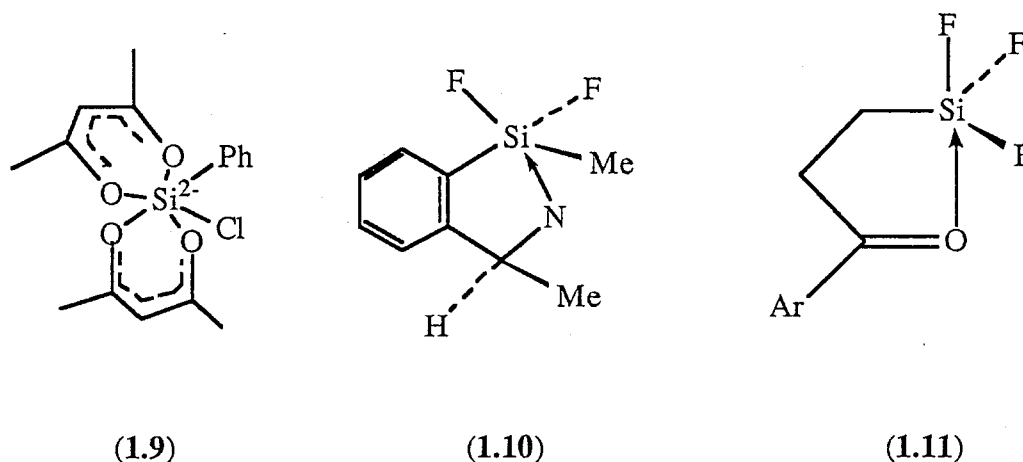
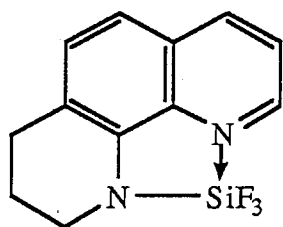
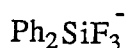


Figure 1.4

by reversible dissociation of the N-Si bond. By contrast Damrauer and Danahey<sup>55</sup> recently extended and repeated <sup>19</sup>F NMR studies initially carried out by Klanberg and Muetterties<sup>47</sup>, and found that **1.13** and **1.14** undergo intramolecular fluorine exchange with  $\Delta G^\ddagger=11.7$  and 9.9 kcal/mol respectively, consistent with pseudorotation or an equivalent mechanism.



(1.12)



(1.13)



(1.14)

In organic chemistry X-ray study has enabled a fuller understanding of reaction mechanism at carbon through the study of intramolecular atomic distances and deviations from tetrahedral geometry<sup>56</sup>. There are a number of X-ray crystallographic studies on organosilicon compounds in which inter- and intramolecular interactions have been revealed.

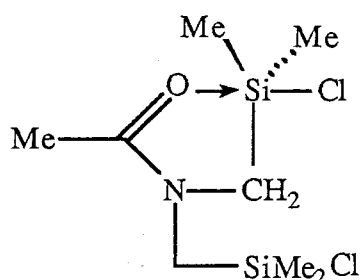
Kemme *et al*<sup>57</sup> have shown that 1-chlorosilatrane (1.15) exhibits intramolecular coordination. The silicon atom in the silatrane has a trigonal bipyramidal geometry with the leaving group Cl and nitrogen atom in axial positions. The nitrogen atom



(1.15)

has pyramidal geometry. The Si-N distance for most silatranes studied varies over 2.02-2.23 Å range, which reflects the extent of transannular interaction which is smaller than the sum of the van der Waals radii of silicon and nitrogen atoms (3.5Å). The Si-N bond length in 1.15 is 2.02 Å and the Si-Cl bond length is 2.15 Å compared with 2.09 Å for chlorotrimethylsilane. For intramolecular complexes

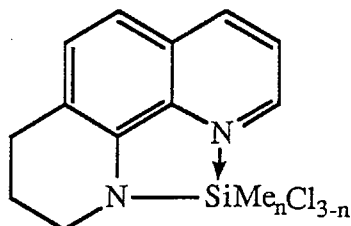
where there is a choice of geometry for two electronegative ligands, the available evidence from X-ray study indicates that they are more likely to be found in apical positions. The geometry of **1.16** has been studied by X-ray crystallography and found five coordination at silicon with distorted trigonal bipyramidal form<sup>58</sup>. The oxygen and chlorine atoms occupy apical sites and the O-Si distance is 1.918 Å. The SiCl bond length for the five-coordinate silicon fragments is 2.348 Å, compared with 2.05 Å for the four-coordinate SiCl bond. The sum of the van der Waals radii



(1.16)

for Si and Cl is 3.80 Å. Although the SiCl bond is lengthened considerably on extra coordination it can still be classified as a covalent bond<sup>59</sup>.

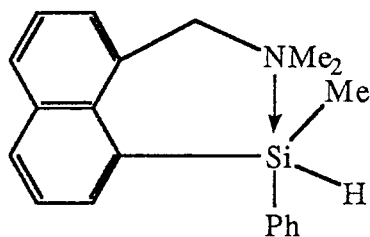
Klebe et al<sup>60,61</sup> have examined the compounds of the type **1.17** and found that the



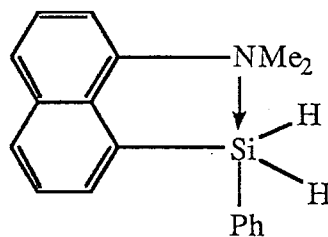
(1.17)



silicon atom in each of the complexes of type **1.17**,  $\text{RSiMe}_2\text{Cl}$ ,  $\text{RSiMeCl}_2$  and  $\text{RSiCl}_3$ , is of trigonal bipyramidal geometry. There is no intramolecular coordination for the  $\text{RSiMe}_3$  derivative **1.17**. The coordinated pyridine-type nitrogen occupies the apical position and the saturated-ring nitrogen, occupies an equatorial position. A chlorine atom is found in the axial position, opposite the coordinated pyridine-type ring. The apical SiCl interatomic distance falls in the order  $\text{RSiMe}_2\text{Cl} > \text{RSiMeCl}_2 > \text{RSiCl}_3$  with respective values being 2.269, 2.207 and 2.15 Å. The pyridine nitrogen-silicon distance follows the same direction and the Si-N<sub>py</sub> distances are  $\text{RSiMe}_2\text{Cl}$ , 2.028;  $\text{RSiMeCl}_2$ , 2.027; and  $\text{RSiCl}_3$ , 1.984 Å. These bond lengths are about 14-18% longer than the equatorial Si-N bonds. Surprisingly the sensitivity to moisture of the chlorosilanes of type **1.17** was reported<sup>60</sup> to decrease in the order  $\text{RSiMe}_2\text{Cl} > \text{RSiMeCl}_2 > \text{RSiCl}_3$  which is the inverse of the expected order. When there is no electronegative 'leaving' group as in compounds **1.18** and



(1.18)



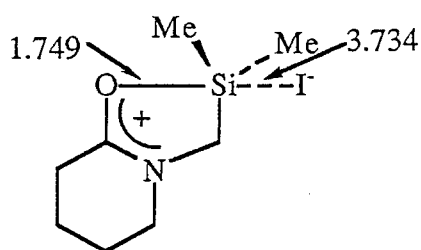
(1.19)

**1.19** there is still significant N-Si bonding, but as expected for silicon bearing no strongly electronegative ligands, the NSi distance is long, 2.26 Å for **1.18**<sup>62</sup>. Hydrogen atoms occupy equatorial positions and the phenyl group is apical in both **1.18** and **1.19**. Substitution of SiH in silanes is strongly favoured over SiMe or SiPh substitution by nucleophilic reagents, and retention of configuration is the predominant stereochemical pathway. The structures of the compounds **1.18** and

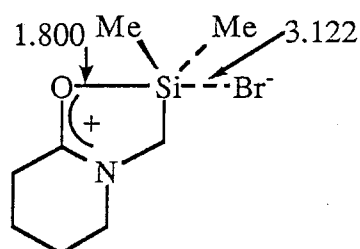
1.19 is evidence that apical entry, probably followed by pseudorotation, is the most efficient pathway for retentive mechanisms<sup>62</sup> and recent calculation by Dieters and Holmes support this view<sup>63,64</sup>.

Burgi<sup>65</sup> was the first to map the reaction pathway of the  $S_N2$  nucleophilic substitution on the basis of X-ray data for complexes with intermediate (tetrahedral vs trigonal bipyramidal) coordination. Later this 'structural correlation' approach was applied to organotin<sup>66</sup> and organosilicon compounds<sup>67-69</sup>. The essence of that method was that bond lengths and angles for a series of structurally related model compounds were compared and used to infer coordination and bond angle changes during the course of a reaction.

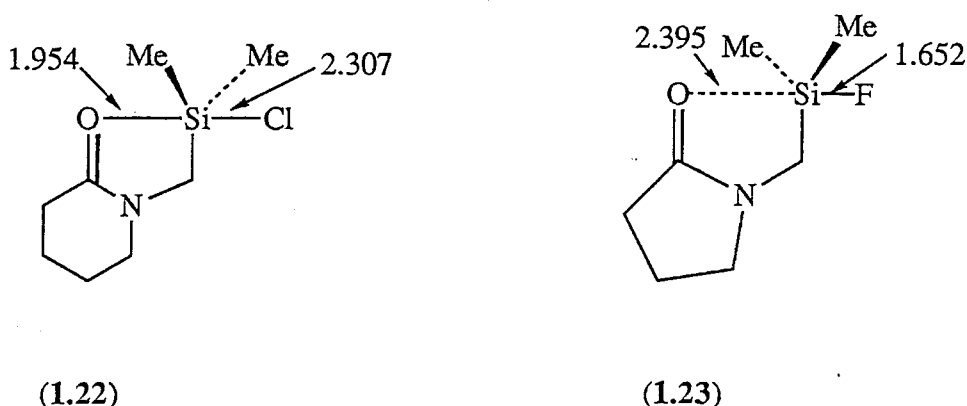
Macharashvili *et al*<sup>70</sup> have used the correlation technique developed by Burgi<sup>65</sup> to analyse a series of crystallographic studies of N-(halogenodimethylsilylmethyl) lactams. Briefly, this method was concerned with an analysis of structural parameters in the solid state complexes as the geometry changes from tetrahedral to trigonal bipyramidal along an  $S_N2$  like reaction profile (Scheme 1.11). Their



(1.20)



(1.21)



Scheme 1.11

X-ray studies showed<sup>70</sup> that Si-O and Si-X (X=I, Br, Cl, F) distances at the pentacoordinate silicon atom in N-(halogenodimethylsilylmethyl)lactams vary over a wide range (1.749-2.395 and 3.734-1.652 Å respectively) in the series X=I→Br→Cl→F. The Si-X interaction changes from ionic (1.20) to covalent (1.23), with weakening the Si-O bond interaction. The IR spectra have shown that on going from iodide to fluoride, the weakening of the Si-O interaction is accompanied by weakening and strengthening of the C=N and C=O bonds respectively. The coordination at silicon atom changes from (4+1, compounds 1.20, 1.21) somewhat distorted tetrahedral through trigonal bipyramidal (3+2, compound 1.22) and back to the distorted tetrahedral, but with inverted, (1+4, compound 1.23) coordination (Scheme 1.11).

Barrow *et al*<sup>67</sup> have used the correlation technique developed by Burgi<sup>65</sup> to analyse a series of crystallographic studies, carried out by various groups. This method is concerned with an analysis of structural parameters in the solid state complexes as the geometry changed from tetrahedral to bipyramidal along an S<sub>N</sub>2 like reaction profile. Figure 1.5 illustrates the parameters used; the  $r(\text{Si} \cdots \text{N})$

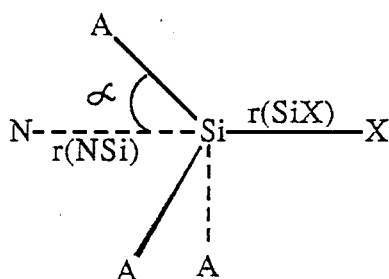


Figure 1.5 Parameters used in the correlation analysis of nucleophilic attack at silicon in an  $S_N2$  like process.

decreases as the intermediate is approached; the  $r(\text{Si-X})$  increases slightly and  $\alpha$  increases. Figure 1.6 shows the scatter plot for a series of silatranes, and other compounds with a long  $\text{Si} \cdots \text{N}$  interaction<sup>67</sup>. It can be seen that as the trigonal bipyramidal geometry is approached,  $r(\text{Si} \cdots \text{N})$  decreases significantly whereas  $r(\text{SiX})$  shows little variation except at  $\alpha = 90^\circ$  which corresponds to true trigonal bipyramidal geometry. The last point refers to the structure of the  $\text{H}_3\text{SiNH}_2$

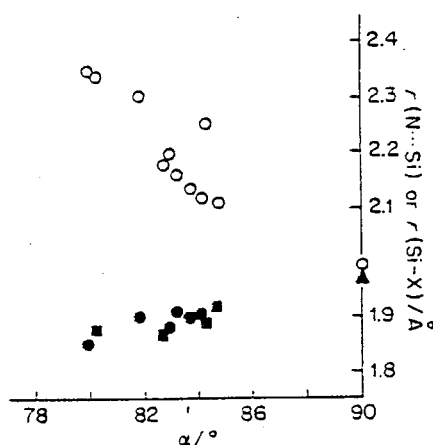
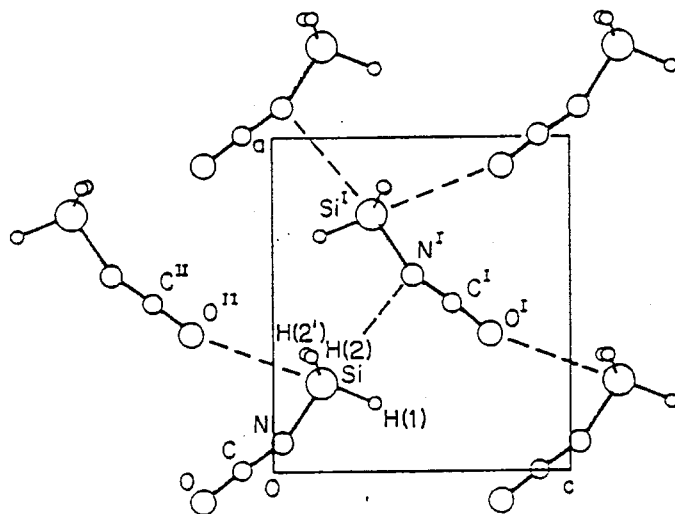


Figure 1.6 Scatter plot of  $r(\text{N} \cdots \text{Si})$ , open circles and  $r(\text{Si-X})$  [ $\text{X}=\text{C}(\text{sp}^2)$  (●),  $\text{C}(\text{sp}^3)$  (■) or  $\text{N}$  (▲)] against  $\alpha$ .

pentamer which has two apical SiN bonds of equal lengths<sup>71</sup>. Figure 1.6 can therefore be taken as an illustration of the reaction pathway leading from tetrahedral four-coordinate silicon to a trigonal, five-coordinated species.

Further X-ray studies on silyl species capable only of intermolecular interactions show similar solid-state complexes in which the coordination number at silicon is extended to five or even six. For example, silyl isocyanate  $\text{H}_3\text{SiNCO}$  exhibits directional intermolecular Si---N and Si-O interactions as illustrated in Figure 1.7<sup>67</sup>. The intermolecular Si---O contact is 330.3 pm and the N-Si--O angle is  $76.7^\circ$ . The N--Si-N angle is  $173.8^\circ$  and the N---Si distance is 331.1 pm. In this example Si--O contact is some 9% less than the sum of the van der Waals radii and the Si---N contact is about 11% less. For disiloxane<sup>72</sup>, disilyl sulphide<sup>73</sup>

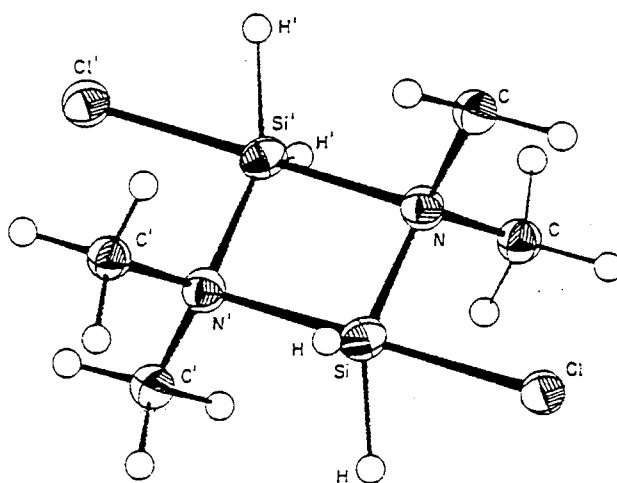


**Figure 1.7** Arrangement of molecules of  $\text{H}_3\text{SiNCO}$  on the mirror plane at  $y=1/4$  showing the N---Si and O---Si interactions.

and disilyl selenide<sup>73</sup> the X-ray structures all showed directional Si---X contacts ( $X=O,S,Se$ ) with the X-Si --X angles close to  $180^\circ$ , and the long Si---X contact being 35-50 pm less than the sum of the van der Waals radii. By contrast the planar trisilylamine shows no tendency to form long, directional Si---N bonds<sup>73</sup>, consistent with its inability to form complexes with  $Me_3B$ <sup>74</sup>.

Chlorosilyl-N, N-dimethylamine in the crystal consists of well separated dimers, as illustrated in Figure 1.8, each dimer being regarded as a 'frozen' intermediate in an  $S_N2$  reaction in which N displaces Cl to form the ionic form of the dimer<sup>75</sup>.

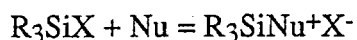
The complexing behaviour of silicon compounds in solution is less well understood



**Figure 1:8** Structure of chlorosilyl-N,N-dimethylamine in the crystal at 116 K.

The  $Si_2N_2Cl$  group is almost planar: the dimer contains a centre of inversion. Bond lengths (pm) and angles (deg): Si-Cl 223.1(6), Si-N 181.4(13), Si-H 149(1), N-C 149.8(18), Si-N 205.4(3), Cl-Si-N 96.1(5), Si-N-C 112.8(9), C-N-C 108.8(14), N-Si-N 83.0(5), Si-N-Si 97.0(6).

than in the solid state. For many silane-nucleophile interactions in which the silane is bonded to a good leaving group the species formed is simply the result of a substitution<sup>76-78</sup>. Where no leaving group is present, infrared studies show the



existence of weak solvent-silicon interactions in trialkoxysilanes<sup>79</sup> and triethylsilane<sup>80</sup>. Trimethylsilylacetate was shown to have a unidentate acetate ligand in solution<sup>81</sup> and tetraacetatosilane formed the hexacoordinate hexaacetate in solution on reaction with acetic anhydride<sup>82</sup>. Organosilicon chlorides<sup>83</sup> and acetates<sup>84</sup> were claimed to form complexes in solution readily with a wide variety of Lewis bases.

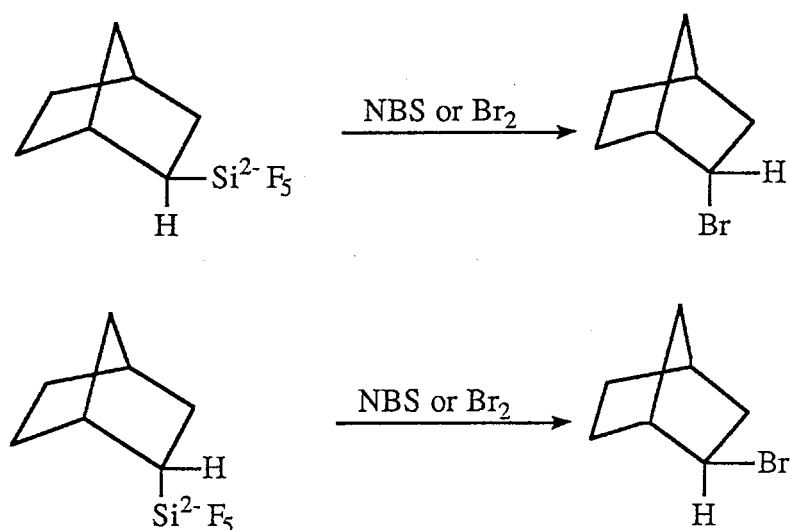
#### **1.4 REACTIVITY OF HYPERVALENT ORGANOSILANES:**

There is much interest in the existence<sup>55,85</sup>, structure<sup>37,38,86</sup>, reactivity<sup>51,87-94</sup> and isomerisation<sup>55,95</sup> of pentacoordinate silicon derivatives that have been proposed as intermediates in reactions of organosilanes in solution<sup>95</sup>. But in spite of the long history of the hypervalent silicon compounds, and the considerable amount of structural investigation devoted to them, relatively little of their chemistry has been explored. There are now however indications that they have a varied chemistry, significantly different from that of their tetravalent counterparts.

The air stable potassium salt,  $K_2SiF_5R$ , which can easily be isolated in pure form has given rise to a number of interesting mechanistic studies concerning the reactivity of these hexacoordinate anions.

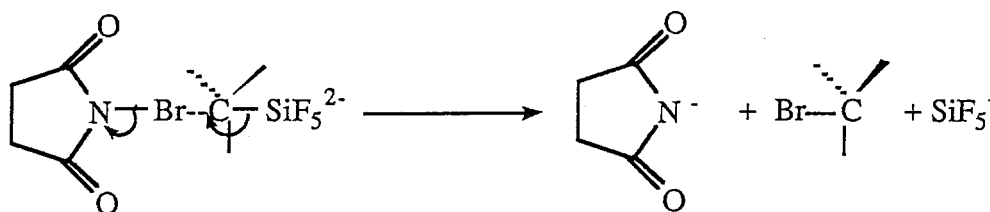
i) Halogenation:

N-Bromosuccinimide, elemental halogen or copper (II) halides induce cleavage of the carbon-silicon bond with the formation of the corresponding organic halide. The reaction of exo- and endo-2 norbornylpentafluorosilicates in polar solvent with

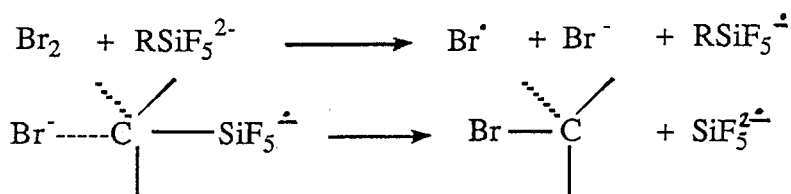


N-bromosuccinimide or bromine gave products in which inversion of configuration had occurred at the carbon atom, with a high degree of selectivity<sup>96</sup>. In non-polar solvents a decrease in yield was observed in the reaction with N-bromosuccinimide, and a loss of stereoselectivity in the reaction of the exo-isomer with bromine. The inversion of configuration with N-bromosuccinimide is due to direct electrophilic displacement (Scheme 1.12), but the reaction with bromine was considered to proceed by an initial electron-transfer step, followed by nucleophilic attack of bromine ion on the resulting organopentafluorosilicate radical ion (Scheme 1.13). Steric constraints or reduction in polarity of the solvent allows dissociation of the radical ion to a free alkyl radical, and loss of stereoselectivity, as observed (Scheme 1.14).

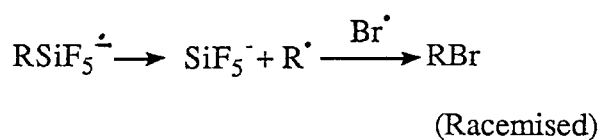




Scheme 1.12

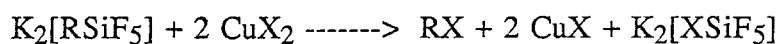


Scheme 1.13

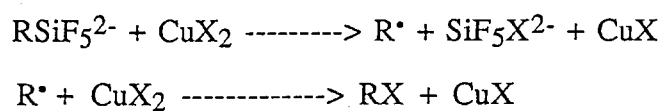


Scheme 1.14

The reaction with copper (II) salts proceeds with complete loss of stereochemistry<sup>97</sup>.



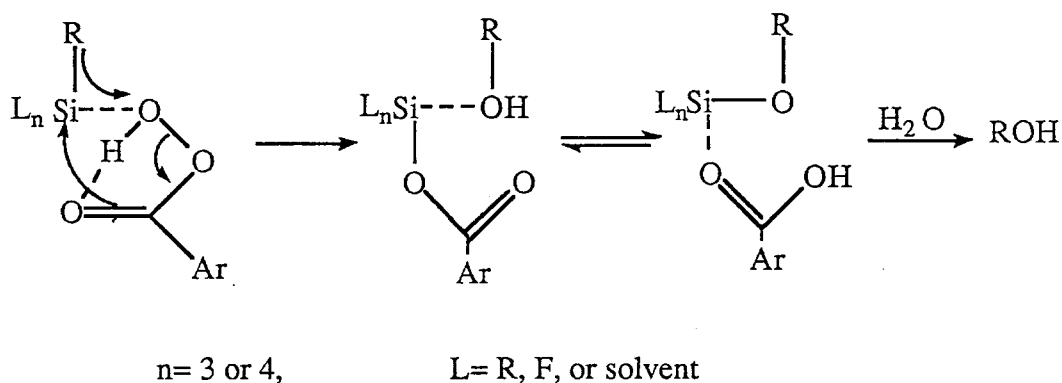
Again, an initial one electron oxidation is postulated, with liberation of a free alkyl radical which undergoes racemisation before conversion to halide (Scheme 1.15).



Scheme 1.15

ii) Oxidation by m-chloroperbenzoic acid:

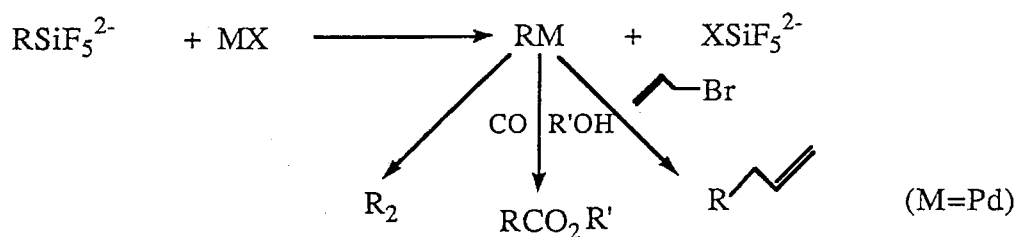
m-Chloroperbenzoic acid oxidises silanes to alcohols by cleaving the carbon-silicon bond. The reaction is stereospecific, and proceeds with retention of configuration. The rate of the reaction is depressed by addition of an excess of potassium fluoride<sup>98</sup>, and the mechanism proposed is shown in Scheme 1.16.



Scheme 1.16

iii) Alkyl transfer:

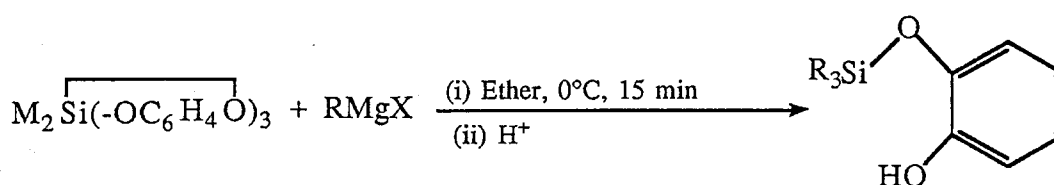
It is found that organopentafluorosilicates reacts with many metal salts e.g. Ag(I), Cu(I) and Pd(II)<sup>99</sup>. The reaction involves alkylation of the metal, and may be followed by reductive coupling of the alkyl groups or carbonylation in case of palladium (Scheme 1.17).



Scheme 1.17

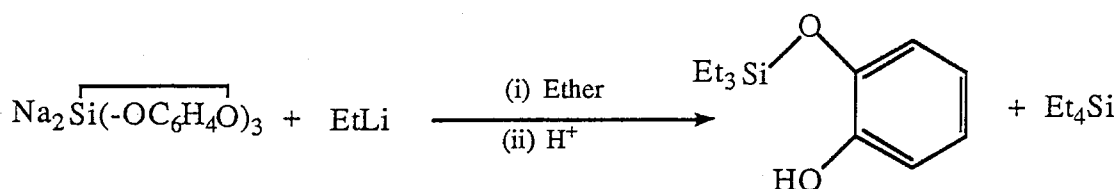
### C) Reactivity of Hexacoordinated Silicon Compounds:

The tris(benzene-1,2-diolato) silicon complexes,  $\text{Si}(-\text{OC}_6\text{H}_4\text{O})_3^{2-} \cdot 2\text{M}^+$  ( $\text{M}=\text{Na}$  or  $\text{K}$ ) were found to react very rapidly with Grignard or organolithium reagents<sup>52,100,101</sup>. The extent of substitution depends on the organometallic

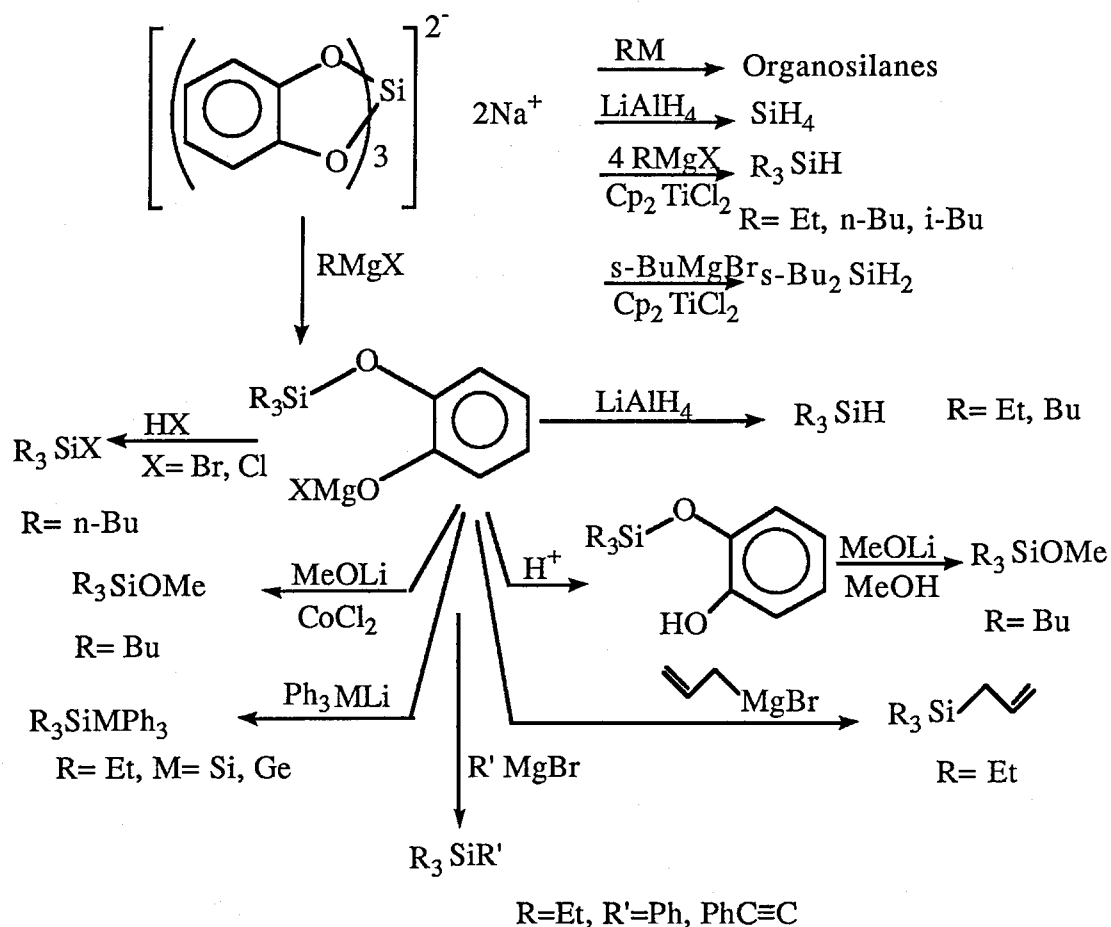


reagent as follows:

- i) When  $\text{RM}$  is an alkyl or benzyl Grignard reagent, three silicon-carbon bonds are formed and this is independent of the ratio of silicon complex/ $\text{RM}$ . (But  $\text{MeMgBr}$  leads only to the formation of  $\text{Me}_4\text{Si}$  in good yield.)
- ii) A mixture of tri- and tetra-organosilanes is obtained when  $\text{RM}$  is an alkylolithium.



iii) When  $\text{RM}$  is an allyl, vinyl, phenyl or alkynyl Grignard reagent, it always gives  $\text{R}_4\text{Si}$ , whatever the ratio silicon complex/ $\text{RM}$ . The intermediate  $\text{R}_3\text{SiOC}_6\text{H}_4\text{OMgX}$  has been treated directly with different reagents leading to various organosilicon compounds<sup>102</sup> shown in Scheme 1.18.



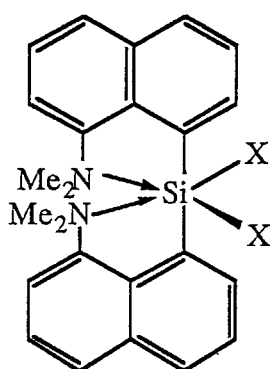
Scheme 1.18

Hexacoordinated silicon complexes have also been treated with a reducing agent such as  $\text{LiAlH}_4$  and  $\text{SiH}_4$  was obtained in quantitative yield. The reaction of  $\beta$ -hydrogenated Grignard reagents activated by  $\text{Cp}_2\text{TiCl}_2$  (Cp=cyclopentadienyl) on tris(benzene-1,2-diolato)silicon complex produces the trisubstituted hydrosilanes (Scheme 1.18).

#### D) Reactivity of Bis(8-(dimethylamino)naphthyl) Complexes of Silicon:

The basic transformations of  $\text{SiF}$ ,  $\text{SiCl}$ , and  $\text{SiH}$  in hexacoordinated silicon species are completely different from those observed with the corresponding tetra- and

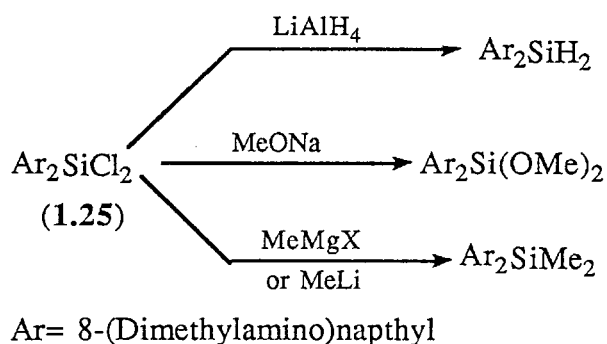
pentacoordinated compounds. Corriu *et al*<sup>103</sup> have found that the reactivities of compounds **1.24** and **1.25** with nucleophiles were different. Difluorosilane (**1.24**) appears to be completely inert to any nucleophilic reagents ( $\text{LiAlH}_4$ ,  $\text{RMgX}$ ,  $\text{RLi}$ ,  $\text{ROH}$ ,  $\text{RONa}$ ), whereas dichlorosilane (**1.25**) is substituted very easily by nucleophiles (Scheme 1.19).



(**1.24**)  $\text{X}=\text{F}$

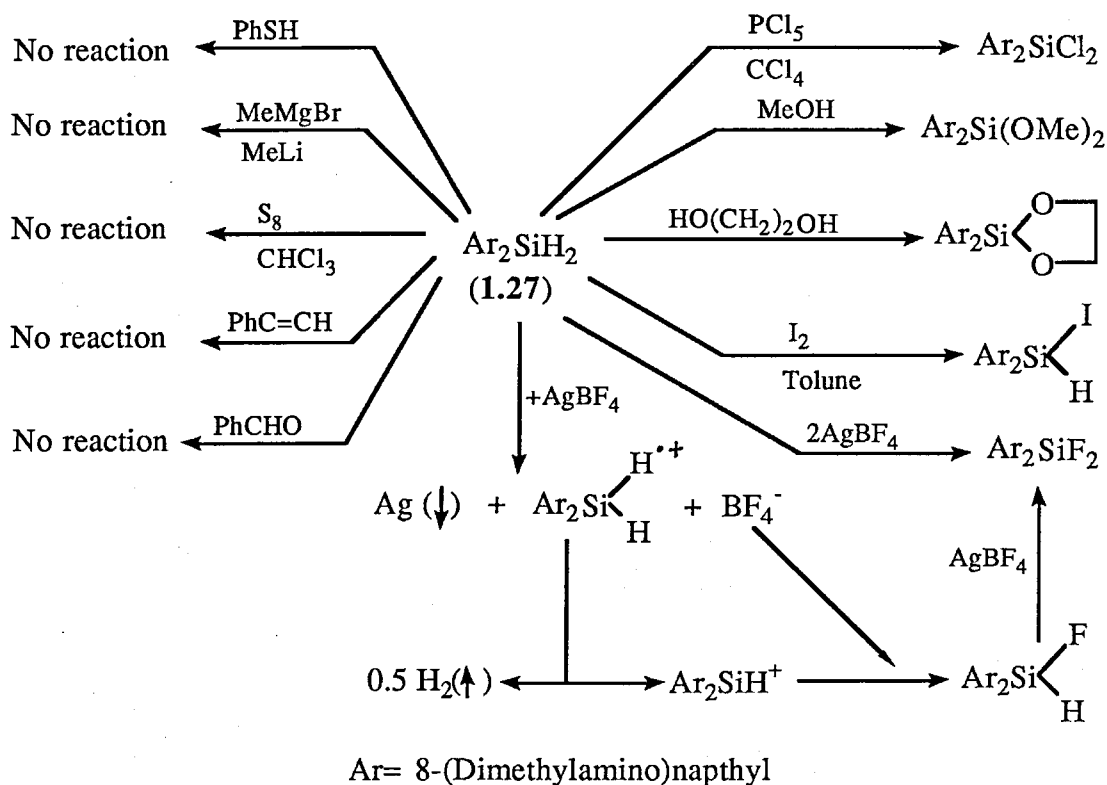
(**1.25**)  $\text{X}=\text{Cl}$

(**1.26**)  $\text{X}=\text{H}$



Scheme 1.19

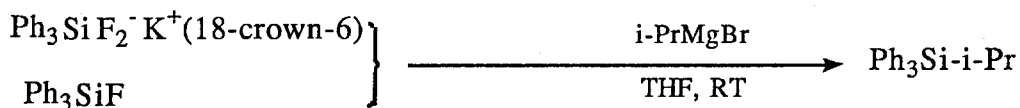
The lack of reactivity of fluorosilane (**1.24**) could be attributed to both the minimal elongation of the  $\text{Si-F}$  bonds and a maximal hindrance around the silicon atom. The reactivity of the hydrosilane (**1.26**) towards nucleophile is again very different from that observed for (**1.24**) and (**1.25**) (Scheme 1.20). It is chemically inert towards strong nucleophiles ( $\text{RLi}$ ,  $\text{RMgX}$ ), whereas organolithium reagents are able to substitute the  $\text{Si-H}$  bond in tetra- and pentacoordinate silicon compounds<sup>104-106</sup>.

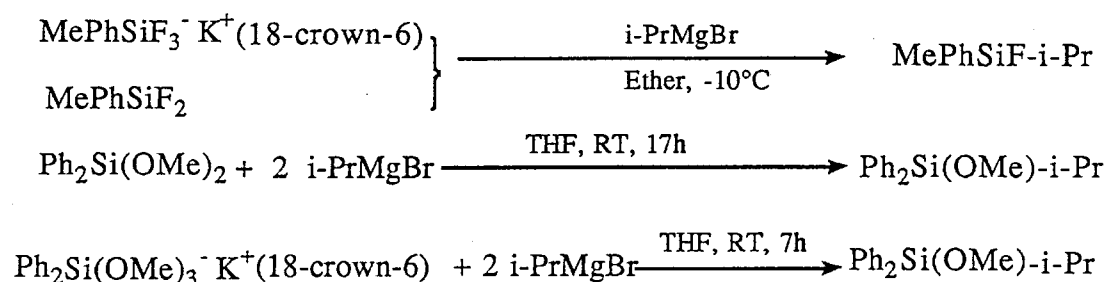


Scheme 1.20

### E) Reactivity of Pentacoordinate Organofluorosilicates and Alkoxysilicates:

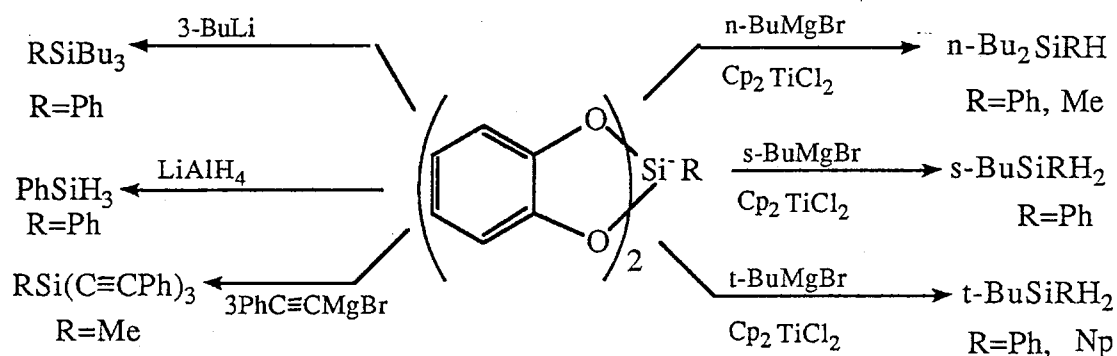
Recent studies<sup>89,107</sup> of the pentacoordinate anionic siliconates,  $\text{Ph}_3\text{Si}^-(\text{OMe})_2\text{K}^+(\text{18-crown-6})$ ,  $\text{Ph}_2\text{Si}^-(\text{OMe})_3\text{K}^+(\text{18-crown-6})$ ,  $\text{Ph}_3\text{Si-F}_2\text{K}^+(\text{18-crown-6})$  and  $\text{MePhSi-F}_3\text{K}^+(\text{18-crown-6})$  have shown that they are very reactive towards strong nucleophiles ( $\text{RMgX}$ ,  $\text{RLi}$ ,  $\text{ROLi}$ ,  $\text{LiAlH}_4$ ) and give the neutral tetravalent substituted silicon derivatives. The pentavalent anionic species was found to be more reactive than the tetravalent analogue towards nucleophile.





F) Reactivity of Organobis(benzene-1,2-diolato) Silicates:

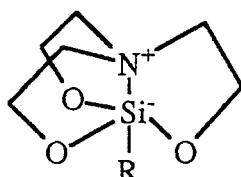
Organobis(benzene-1,2-diolato) silicon complexes  $\text{Na}^+[\text{RSi}(-\text{OC}_6\text{H}_4\text{O})_2]^-$  were found to be very reactive towards organometallic reagents and hydrides<sup>51</sup>. An excess of hydride leads to trihydrogenosilanes. Reaction with three moles of organolithium reagent or allyl and alkynyl magnesium bromide leads to the tetrasubstituted product. A one-pot procedure for the synthesis of hydrosilane has been reported<sup>108</sup> using alkylmagnesium bromide activated by  $\text{Cp}_2\text{TiCl}_2$ . Primary Grignard reagents lead to monohydrosilanes while secondary and tertiary Grignard reagents lead to dihydrosilanes (Scheme 1.21).



Scheme 1.21

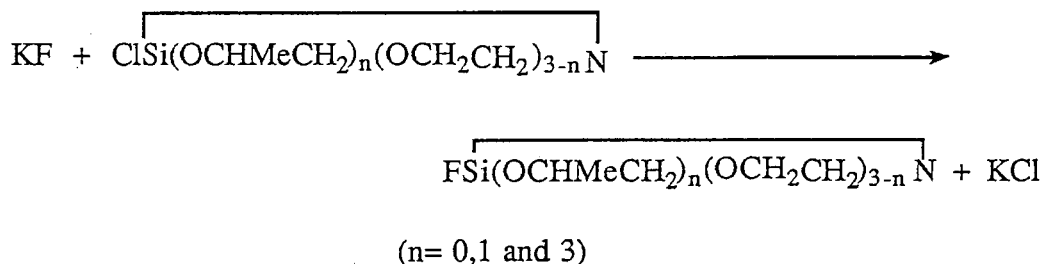
### G) Reactivity of Silatranes:

Silatranes (1.27)<sup>109,110</sup> (cyclic organosilicon ether of tris(2-oxyalkyl)amines) and their derivatives constitute a class of neutral pentacoordinate silicon compounds by virtue of the transannular interaction between the silicon centre and the nitrogen



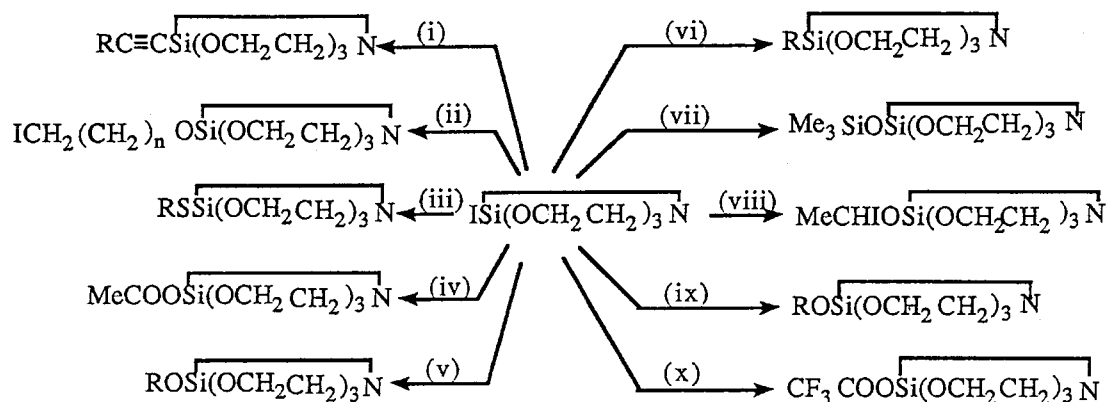
(1.27)

group. Frye *et al*<sup>111</sup> first reported the conversion of 1-chlorotribenzosilatranes to 1-aryloxy derivatives with phenols. Voronkov and coworkers<sup>112</sup> have performed an exchange reaction of 1-chlorosilatranes with potassium fluoride in HMPA which gives the corresponding fluoro derivatives.



The NMR data has shown<sup>112</sup> that the Si-I bond in 1-iodosilatranes is highly polarized which suggests that this compound is more electrophilic than trimethyliodosilane. This compound has been treated directly with different reagents leading to various organosilicon compounds<sup>113-116</sup> as shown in Scheme 1.22.





(i)  $\text{RC}\equiv\text{CH}$ ; (ii)  $\text{CH}_2(\text{CH}_2)_n\text{O}$ ; (iii)  $\text{RSM}$ ,  $\text{M}=\text{H}$ ,  $\text{Na}$ ; (iv)  $\text{MeCOOEt}$ ; (v)  $\text{ROM}$   
 $\text{M}=\text{H}$ ,  $\text{Na}$ ; (vi)  $\text{RR}^1\text{Hg}$ ; (vii)  $(\text{Me}_3\text{Si})_2\text{O}$ ; (viii)  $\text{MeCHO}$ ; (ix)  $\text{ROR}^1$ ;  
 (x)  $(\text{CF}_3\text{CO})_2\text{O}$

Scheme 1.22

Corriu *et al*<sup>117</sup> have reported the reactions of hydro, organyl and halosilatrane with organolithium and organomagnesium reagents. The reactivity of hydrosilatrane with different nucleophiles are shown in Table 1.1. The order of reactivity of nucleophilic reagents was  $\text{nBuLi}/12\text{-crown-4} \gg \text{nBuLi} > \text{nBu}_2\text{Mg} \approx \text{nBuMgBr}$ . Cleavage of the equatorial bonds occurs more readily than that of the apical Si-H bonds.

**Table 1.1** Reactions of hydrosilatrane with organometallic compounds in THF

Entry	Reagents (molar equivalent)	Temp (°C)	Time (h)	Yield (%)	
				R <sub>3</sub> SiH	R <sub>4</sub> Si
1	nBuLi (5)	20	1	66	22
2.	nBuLi (3.2)	20	1	90	10
3	nBuLi (3.2)	0	24	62	-
4	nBuLi (2)	20	24	34	-
5	nBuLi (1)	20	24	24	-
6	nBuLi/12-crown-4 (3.2)	-50	1	87	-
7	nBuLi/12-crown-4 (3.2)	-78	24	84	2
8	nBuMgBr (3.2)	20	24	78	-
9	nBu <sub>2</sub> Mg (3.2)	20	24	81	-
10	PhLi (5)	20	20	-	68

They have also shown<sup>117</sup> that a fairly high yield of tetraorganosilane was obtained when nBuLi was treated with various organylsilatranes (Table 1.2). With vinylsilatrane there was simultaneous substitution of the Si-O bonds and addition of nBuLi to the C=C bond (entry 4), while tBuLi involves only addition to the C=C bond at -78°C, with no attack on the silatrane ring (entry 5).

**Table 1.2** Reactions of organylsilatranes with an excess of an organometallic reagent (3.5 molar equivalents) in THF

Entry	R	Reagent	Temp. (°C)	Time (h)	Product	Yield (%)
1	nBu	$\text{CH}_2=\text{CH}-\text{MgBr}$	30	4	${}^n\text{BuSi}(\text{CH}_2=\text{CH})_3$	70
2	nBu	${}^n\text{BuLi}$	20	4	${}^n\text{Bu}_4\text{Si}$	70
3	$\text{CH}_2=\text{CH}-\text{CH}_2$	${}^n\text{BuLi}$	20	0,5	$\text{CH}_2=\text{CH}-\text{CH}_2\text{Si}^n\text{Bu}_3$	61
4	$\text{CH}_2=\text{CH}$	${}^n\text{BuLi}$	20	0,5	$\begin{cases} {}^n\text{Bu}-\text{CH}_2-\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N} \\ {}^n\text{Bu}-\text{CH}_2-\text{CH}_2\text{Si}^n\text{Bu}_3 \end{cases}$	17 30
5	$\text{CH}_2=\text{CH}$	${}^t\text{BuLi}$	-78	2,5	${}^t\text{Bu}-\text{CH}_2-\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$	81
6	Ph- $\text{CH}_2$	${}^n\text{BuLi}$	20	4	Ph- $\text{CH}_2\text{Si}^n\text{Bu}_3$	75
7	Ph- $\text{CH}_2\text{CH}_2$	${}^n\text{BuLi}$	20	4	Ph- $\text{CH}_2\text{CH}_2\text{Si}^n\text{Bu}_3$	92

Chloro- and bromosilatranes were found to react with nBuLi to give, after reduction with  $\text{LiAlH}_4$ , tri-n-butylsilane as the major product even in presence of excess nBuLi (Table 1.3). A poor yield of  ${}^n\text{Bu}_4\text{Si}$  was obtained from reaction of an excess of nBuLi on chlorosilatrane after prolonged reaction (entry 3).

**Table 1.3** Reactions of halosilatranes  $\text{XSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  with nBuLi in THF followed by  $\text{LiAlH}_4$  reduction

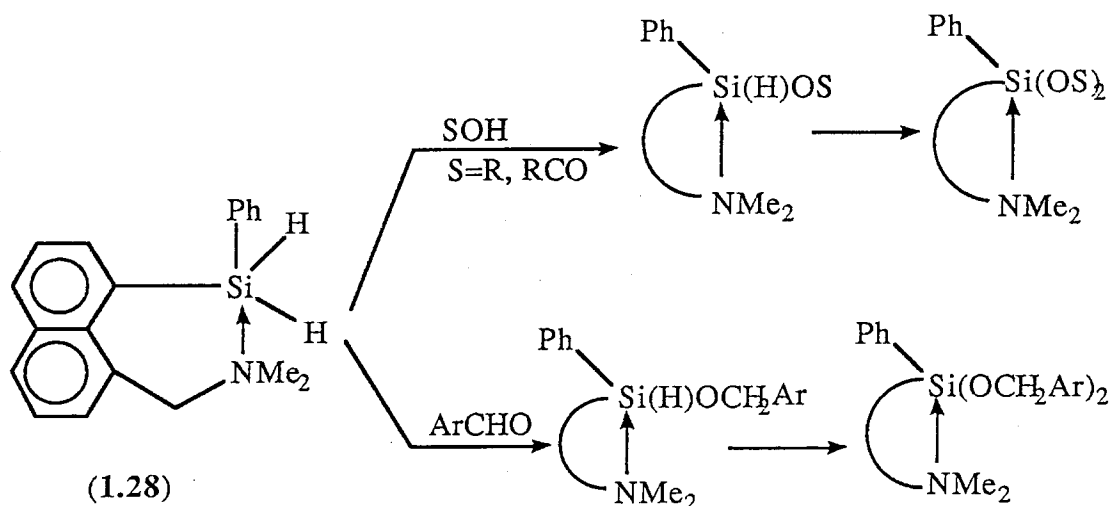
Entry	X	Reagent (molar equivalents)	Temp. (°C)	Time (h)	Yield (%)	
					nBu <sub>3</sub> SiH	nBu <sub>4</sub> Si
1	Cl	nBuLi (1)	20	24	6	<1
2	Cl	nBuLi (3.2)	20	24	56.4	2.5
3	Cl	nBuLi (5.5)	20	48	74	10
4	Br	nBuLi (3.2)	20	24	44	2.5

### H) Neutral Pentacoordinated Silicon Hydrides as Reducing Agents:

Eaborn *et al*<sup>118</sup> have suggested that hydrosilatrane can act as reducing agents for carbonyl compounds and organic halides, in contrast to tetracoordinated hydrosilanes, which do not exhibit any reactivity towards alcohols, acid or carbonyl groups.

The hydrosilane(1.28) exhibits high reactivity towards alcohols, acids and carbonyl groups without any activation. (Scheme 1.23)<sup>119</sup>. Under the same conditions tetracoordinate dihydrosilanes do not react at all.

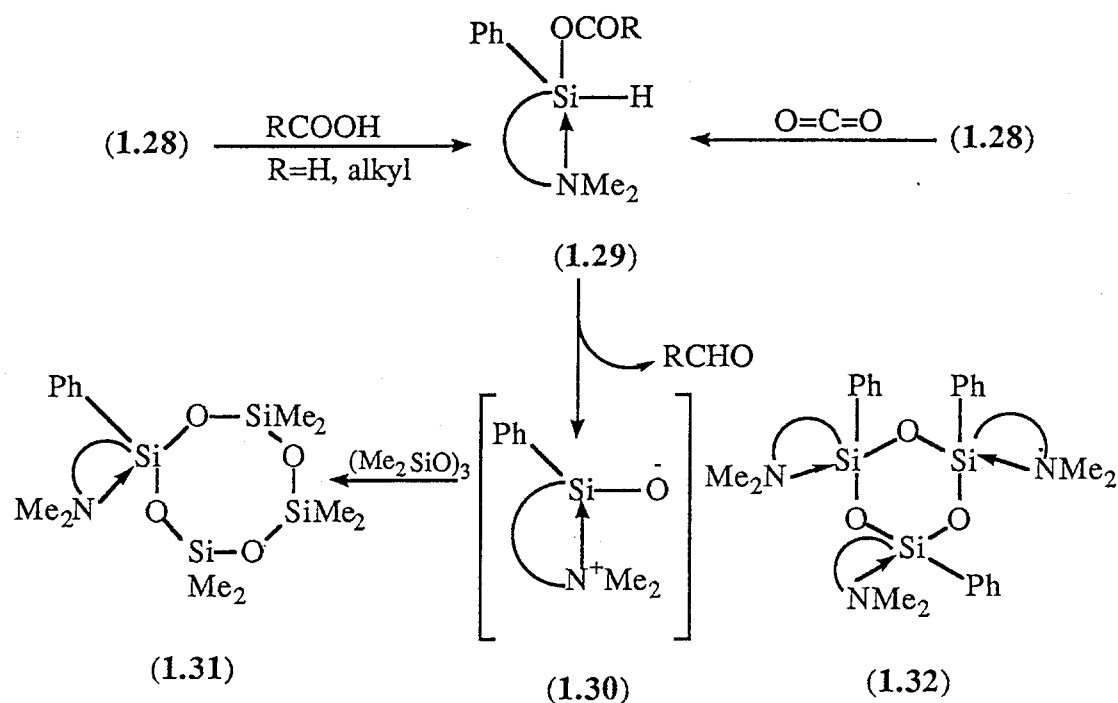
Reaction of 1.28 with carbon dioxide is facile and from which the silyl ester of formic acid 1.29 has been isolated and characterised. The same compound was obtained from the reaction of 1.28 with formic acid. The thermal decomposition of



Scheme 1.23

this ester gave  $\text{H}_2\text{C}=\text{O}$  and trisiloxane (1.32). When the reaction was performed in the presence of hexamethylcyclotrisiloxane, the adduct 1.31 corresponding to insertion of the silanone into the Si-O bond was observed.

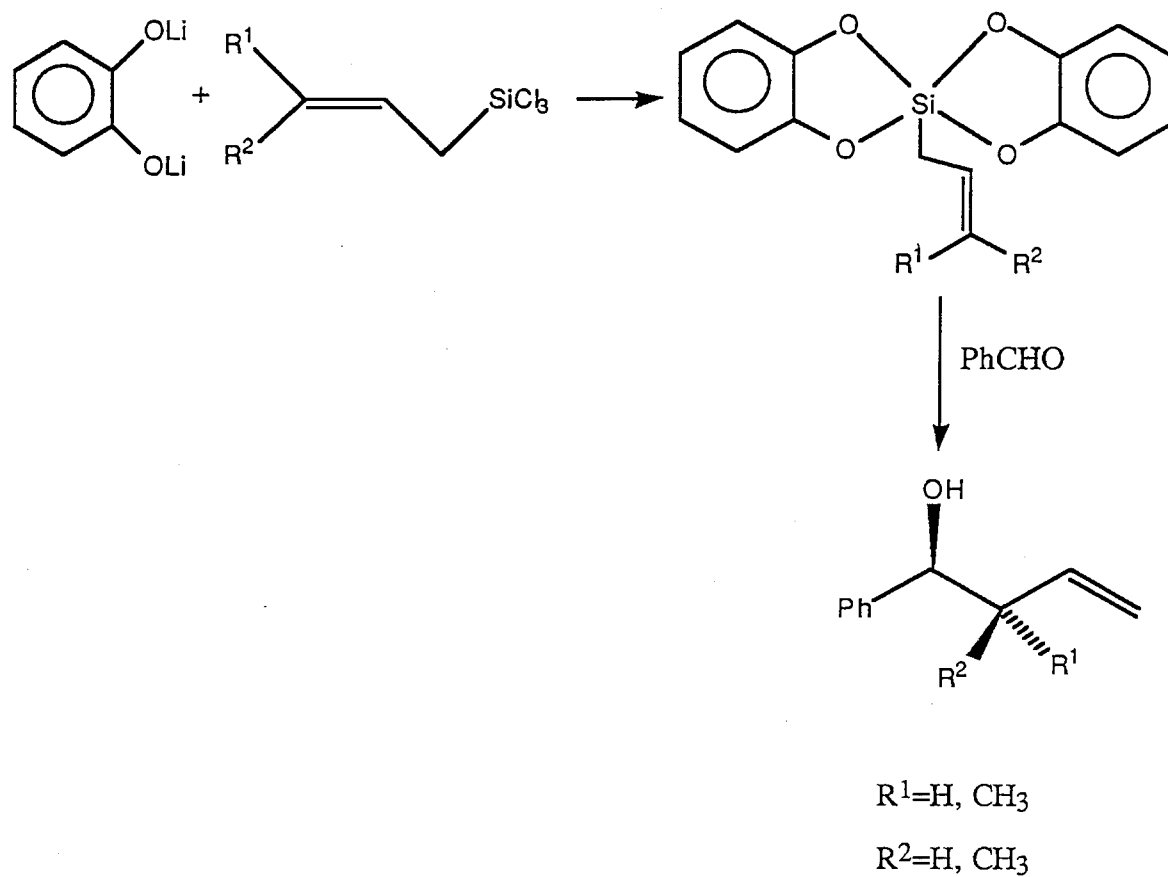
The mechanism proposed is shown in Scheme 1.24. Formation of silanone (1.30) from hypervalent silicon compound 1.29 is proven by formation of 1.31 and 1.32.



Scheme 1.24

i) Reaction of pentacoordinate allylsilicates with aldehydes

Kira *et al*<sup>120</sup> have found that lithium salts of bis(1,2-benzenediolato)allylsilicates react with aromatic aldehydes chemoselectively to give the corresponding homoallyl alcohols in a regiospecific and highly diastereoselective manner. They synthesised the allyl silicates by treating allylchlorosilane and dilithium catecholate as shown in Scheme 1.25.



Scheme 1.25

They proposed a six-membered cyclic transition state formed due to enhanced nucleophilicity of the  $\gamma$ -carbon of the allylsilicates as well as by the significant Lewis acidity giving hexacoordinate silicates as shown in Figure 1.9

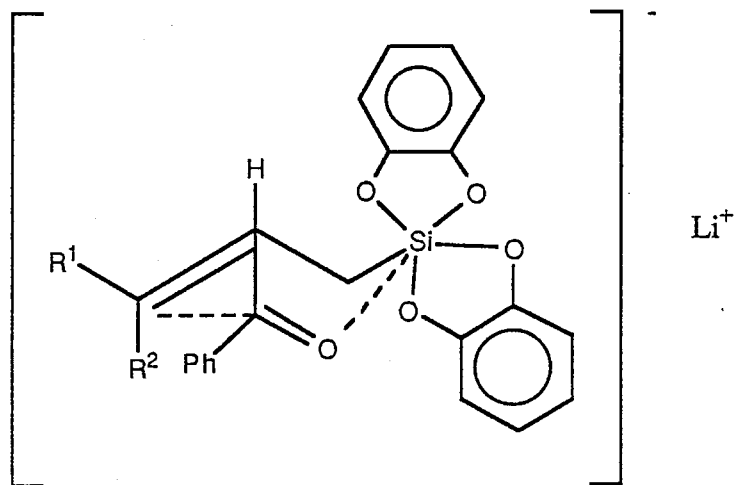


Figure 1.9

There is now a significant body of evidence suggesting that silanes can be activated by coordination which enhance the electronegative, electrophilic character of the remaining substituents whilst increasing the electrophilicity of the silicon atom.

## ***SECTION A***

***An NMR Spectroscopic Method for Mapping Reaction in Solution***



## 2.1A INTRODUCTION:

Burgi<sup>65</sup> was the first to map the reaction pathway of the  $S_N2$  nucleophilic substitution on the basis of X-ray data for complexes with intermediate (tetrahedral vs trigonal bipyramidal) coordination. Later this 'structural correlation' approach was applied to organotin<sup>66</sup> and organosilicon compounds<sup>67-69</sup>. The essence of the method is that bond lengths and angles for a series of structurally related model compounds were compared and used to infer coordination and bond angle changes during the course of a reaction.

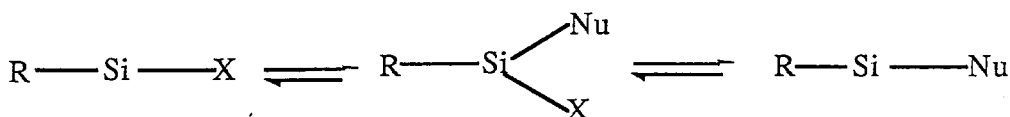
As described in chapter one Macharashvili *et al*<sup>70</sup> have used the correlation technique developed by Burgi<sup>65</sup> to analyse a series of crystallographic studies of N-(halogenodimethylsilylmethyl) lactams. Briefly, this method consisted of an analysis of structural parameters in the solid state complexes as the geometry changes from tetrahedral to trigonal bipyramidal along an  $S_N2$  like reaction profile. Their<sup>70</sup> X-ray studies showed that Si-O and Si-X (X = I, Br, Cl, F) distances at the pentacoordinate silicon atom in N-(halogenodimethylsilylmethyl)lactams vary over a wide range (1.749-2.461 and 3.734-1.652 Å respectively) in the series X = I → Br → Cl → F. The coordination at the silicon atom changed from (4+1, when X = I, Br) i.e., somewhat distorted tetrahedral through trigonal bipyramidal (3+2, when X = Cl), and back to the distorted tetrahedral, but with inverted, (1+4, X = F) coordination.

We sought to develop a method that would enable the progress of a particular reaction to be mapped *in solution* by preparing series of compounds that represent species 'frozen' at various points on the reaction profile. Whereas X-ray

crystallography gives very detailed structural information, solution studies will necessarily be more qualitative. Nevertheless we have produced a system in which the progress of a nucleophilic substitution from reactants to products, through intermediates, can be monitored in solution by studying  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR data in a reasonably quantitative manner.

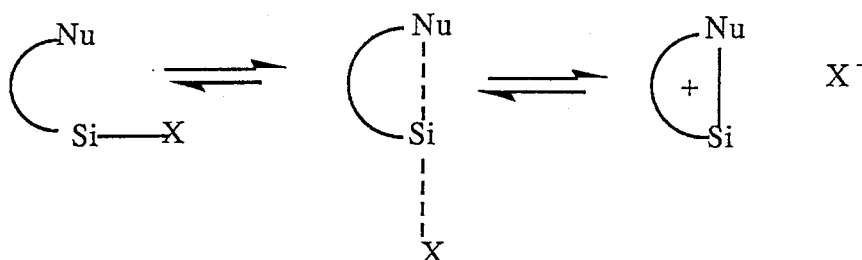
## 2.2A RESULTS AND DISCUSSION:

For a system  $\text{R-Si-X}$  undergoing substitution to  $\text{R-Si-Nu}$  in reaction (Scheme 2.1A) the minimum requirements for studying the progress of reaction are i) a measure of the extent of Nu-Si bond formation (and or Si-X bond breaking) and ii) a measure of the coordination state of the nucleus Si.



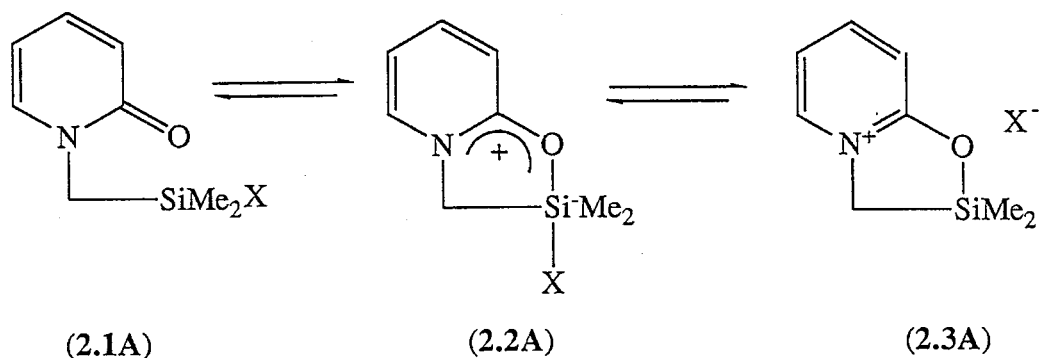
Scheme 2.1A

The coordination state of Si can usually be determined from the chemical shift of Si. The extent of Nu-Si bond making is more difficult to measure. In a chelating system, Scheme 2.2A, the extent of coordination of Nu can be estimated with some



Scheme 2.2A

accuracy if it is accompanied by a significant change in the nature of the molecule, as for example in an aromatization. We chose, the 2-pyridone molecule which can undergo the following changes (Scheme 2.3A).



Scheme 2.3A

Compounds (2.1A), (2.2A) and (2.3A) could be in equilibrium as shown in Scheme 2.3A, but it is possible that there is a continuum of structures of which 2.1A, 2.2A and 2.3A represent the extremes as the O-Si bond is made and the Si-X is broken. The major assumption is that, as the reaction progresses from 2.1A to 2.3A the NMR chemical shifts in the ring can be closely approximated by the chemical shifts of an appropriate mixture of the model compounds such as (2.4A) and (2.5A).

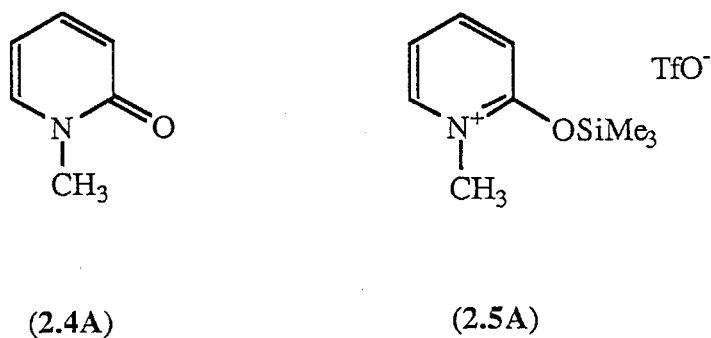
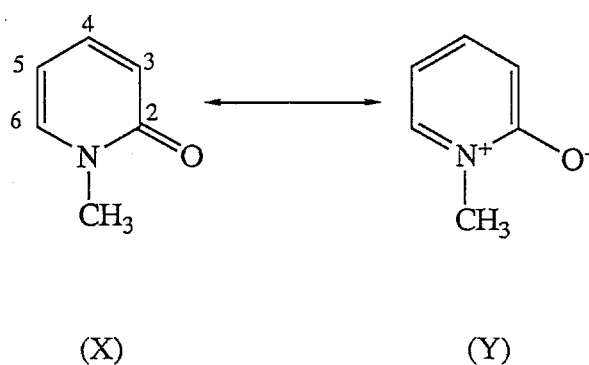
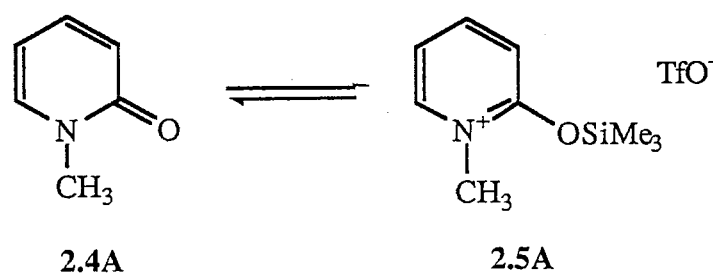


Figure 2.1A and Table 2.1A shows the  $^{13}\text{C}$  NMR chemical shifts changes as N-methyl-2-pyridone, **2.4A** in  $\text{CDCl}_3$ , was titrated with successive amounts of trimethylsilyltriflate ( $\text{Me}_3\text{SiOTf}$ ) to give **2.5A**. N-Methyl-2-pyridone can be thought of as a cyclic amide or as an N-substituted pyridine. It can be drawn in two tautomeric forms (Scheme 2.4A) although the oxo tautomer (Scheme 2.4AX) is the predominant one<sup>121</sup>.



Scheme 2.4A

The proton and carbon-13 NMR chemical shift changes that occur in N-methyl-2-pyridone, as a result of silylation by trimethylsilyltriflate are shown in Table 2.1A. There was an equilibrium between the silylated pyridone and the pyridone when 0.6 equivalent of trimethylsilyltriflate was added to N-methylpyridone as shown in Scheme 2.5A. The equilibrium was fast on the NMR time scale, so we observed only one set of signals in the carbon-13 NMR between the two extremes.

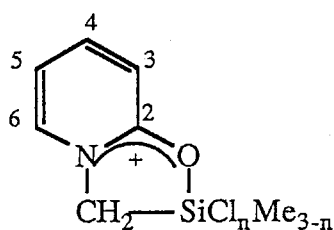


Scheme 2.5A

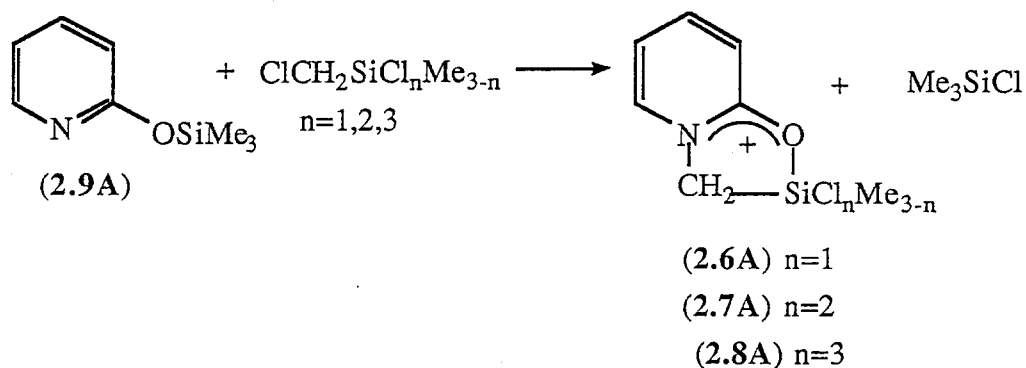
A general deshielding was observed in the proton and carbon spectra except for C-3 and C-2. The carbonyl carbon was substantially shifted to high field in the silylated species, implying that the double bond character of the carbonyl group has been reduced. The variation of the chemical shift observed in the remaining carbons may be rationalised by assuming that the positive charge produced by silylation was delocalised, mesomerically and inductively, into the ring system, the inductive effect being more pronounced at those carbon atoms which are closer to the amide moiety.

When successive amounts of trimethylsilyltriflate was added to N-methylpyridone, there was an equilibrium between the pyridone and silylated pyridone as shown in Scheme 2.5A. The silicon-29 chemical shift was same for all the ratios of pyridone:silane up to 1:1 which showed that a) there was only one silicon environment during the process of silylation as complete silylation occurred at all mole ratios and b) equilibrium between 2.4A and 2.5A is rapid on the NMR time scale. There was therefore only one resonance for each of the carbon atoms C-2, C-3, C-4, C-5 and C-6 in any mixture of 2.4A and 2.5A. There was a very good linear correlation between the chemical shifts of the carbon nuclei in a mixture of 2.4A and 2.5A and the mole fraction of 2.5A (Figure 2.1A).



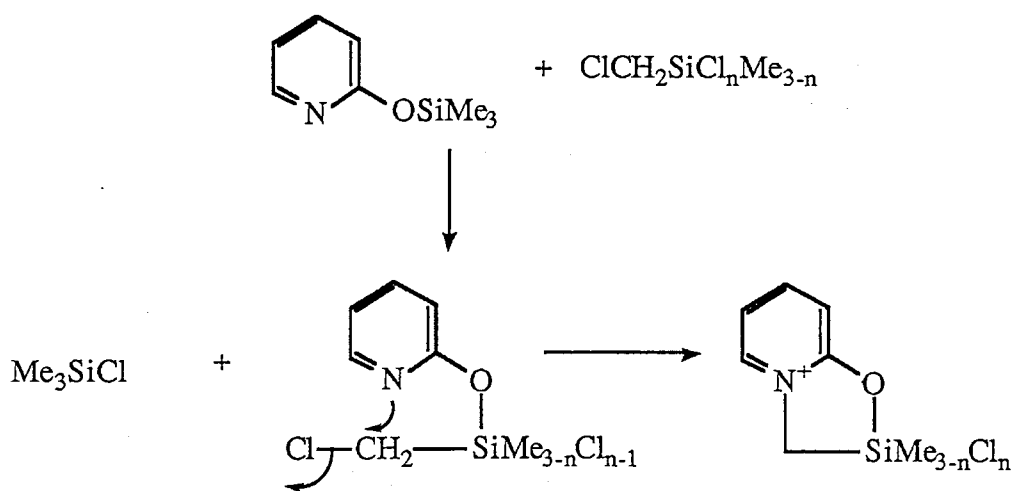
(2.6A)  $n=1$ (2.7A)  $n=2$ (2.8A)  $n=3$ 

When 2-trimethylsiloxy pyridine (2.9A) was treated with chloromethylchlorosilane ( $\text{ClCH}_2\text{SiCl}_n\text{Me}_{3-n}$ ), 2-pyridone derivatives (2.6A-2.8A) were obtained, with liberation of one equivalent of chlorotrimethylsilane (Scheme 2.6A).



Scheme 2.6A

A similar mechanism like the synthesis of (O-Si)chloro[1-(1,1-dimethyl-2-acylhydrazonium)methyl]dimethylsilanes from O-trimethylsilyl derivatives of carboxylic acid 1,1-dimethylhydrazides with chloromethyldimethylchlorosilane<sup>129</sup> can be put forward for the formation of our pyridone derivatives as shown in Scheme 2.7A.



Scheme 2.7A

There is ample evidence from X-ray crystallography that chelated amide complexes of dimethylchlorosilanes are five coordinated with bond orders of about 0.5 for both Si-O and Si-Cl bonds<sup>70</sup>.

The chemical shifts of the ring carbon nuclei in **2.6A** in  $\text{CD}_3\text{CN}$  (C-2, 160.1; C-3, 115.8; C-4, 139.3; C-5, 113.6; C-6, 143.3) resembled closely those of an equimolecular mixture of **2.4A** and **2.5A** with chemical shifts differing by less than  $\pm 1$  ppm. from those in the mixture. This corresponded to an “extent of reaction” of about 50% for compound **2.6A**. There was an excellent correlation with C-5 and C-6 chemical shifts where the differences between **2.4A** and **2.5A** were greatest and a fair correlation with C-3 and C-4 (Table 2.2A). The correlation with C-2 was generally poor for chelated compounds such as **2.6A-2.8A**.

Table 2.2A Carbon-13 chemical shifts ( $\delta$  ppm) of compounds **2.4A-2.6A**.

Compound	C-2	C-3	C-4	C-5	C-6
<b>2.4A</b>	162.8	120.0	139.1	105.6	139.7
<b>2.6A</b>	160.1	115.8	140.0	113.6	143.3
<b>2.5A</b>	157.2	114.0	143.8	119.0	148.0



The  $^{29}\text{Si}$  NMR spectrum of **2.6A** was a sharp single resonance at about -41 ppm, which was the evidence of pentacoordination at silicon<sup>39</sup>. The silicon-29 chemical shift for  $\text{Me}_3\text{SiCl}$  is 35.0 ppm and we therefore observed about 70 ppm upfield in compound **2.6A** relative to the expected shift for a four coordinate chlorosilane. The  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra of **2.6A** were temperature independent (Table 2.3A) and a solution of **2.6A** in acetonitrile does not conduct electricity. The compound

Table 2.3A Variable temperature NMR Data for chlorodimethylsilylmethylpyrid-2-one (2.6A)

$\delta$ (ppm)		Temperature ( $^{\circ}\text{C}$ )		
		RT	-50	+50
$^1\text{H}$	H-3	6.9	6.9	6.9
	H-4	7.9	7.9	7.9
	H-5	6.8	6.7	6.7
	H-6	7.7	7.6	7.6
	NCH <sub>2</sub>	3.7	3.7	3.7
	SiMe	0.64	0.63	0.65
$^{13}\text{C}$	C-2	160.1	160.0	160.0
	C-3	115.8	113.6	113.6
	C-4	140.0	139.3	139.3
	C-5	113.6	115.7	115.7
	C-6	143.3	143.3	143.2
	NCH <sub>2</sub>	42.2	42.1	42.2
	SiMe	7.5	7.5	7.5
$^{29}\text{Si}$	SiMe	-41.1	-41.0	-41.0

Quantities used:

(**2.6A**) : 2 mmol

Solvent :  $\text{CDCl}_3 + \text{CD}_3\text{CN}$ , 1:1, 2 ml

2.6A being unequivocally five coordinate at silicon confirmed that the changes in the  $^{13}\text{C}$  NMR pyridone ligand with increasing O-Si coordination was consistent with those observed for a 2.4A, 2.5A equilibrium or intermediate species. For 2.6A, the O-Si bond was about 50% formed and the structure corresponded to 2.2A (Scheme 2.3A).

It is well established that the tendency to five coordination increases in the order  $\text{R}_3\text{SiCl} < \text{R}_2\text{SiCl}_2 < \text{RSiCl}_3$ <sup>68</sup>. The expectation for the series 2.6A-2.8A was that as *n* increases, the O-Si and Si-Cl apical bond lengths would decrease<sup>60</sup> as the complexes increasingly resembled stable five coordinate compounds with all bond orders approaching unity. The  $^{13}\text{C}$  NMR chemical shifts of 2.7A in  $\text{CDCl}_3$  (C-2, 162.2; C-3, 114.5; C-4, 139.0; C-5, 113.9; C-6, 144.8) suggested about 65% bond formation, and those of 2.8A in  $\text{CDCl}_3$  (C-2, 160.8; C-3, 114.0; C-4, 140.0; C-5, 115.4; C-6, 146.1) about 75% O-Si bond formation. Figure 2.2A shows the

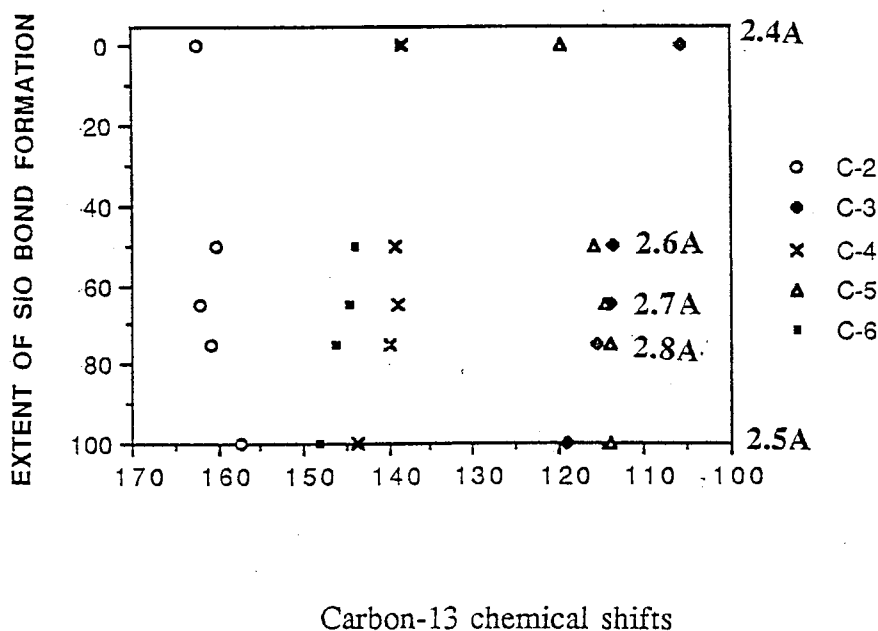
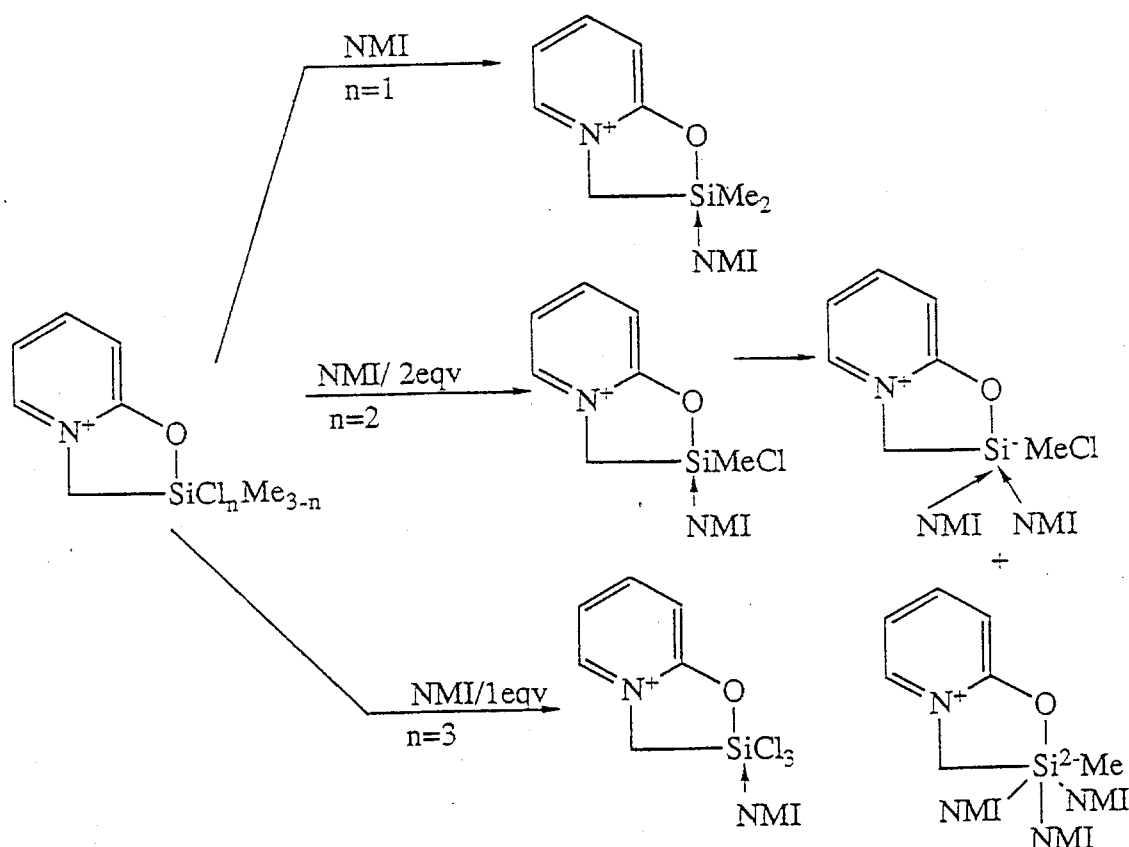


Figure 2.2A Extent of Si-O bond formation for compounds 2.4A-2.8A

variation in O-Si bond formation for the series 2.6A-2.8A. The  $^{29}\text{Si}$  NMR Chemical shifts -52.4 and -77.7 ppm for 2.7A and 2.8A respectively were entirely consistent with fully pentacoordination at silicon.

It has also been observed that as the extent of reaction increases from 2.6A-2.8A while maintaining the five coordination at silicon, the silicon atom becomes more susceptible to addition than substitution. Addition of N-methylimidazole (NMI) to 2.6A gave a substitution product (Table 2.4A), while NMI with 2.8A gave the hexacoordinate addition product (Table 2.5A). When one equivalent of NMI was added to 2.7A, a peak at -72.9 in  $^{29}\text{Si}$  NMR was observed and assigned as due to substitution. An additional peak at -160.5 ppm was observed when 2 equivalent of NMI was added, and it was assigned for hexavalent silicon atom, (Table 2.6A) formed due to addition of NMI to the silicon atom as shown in Scheme 2.8A.



Scheme 2.8A

These preliminary studies show that the mapping of nucleophilic substitution at Si in solution can therefore be modelled by studying the NMR spectra of a series of compounds **2.1A** in which X is varied and substituents may be placed in the ring to modify the nucleophilicity of the oxygen atoms. For each compound the extent of O-Si bond-making can be determined and the coordination state of Si may also be estimated. With a sufficiently large number of compounds a picture of the bond making and coordination changes during a reaction may therefore be assembled. In the next section we show how this new method has been applied to map the structure of complexes in the series **2.1A**, **2.2A**, **2.3A** during nucleophilic substitution at  $\text{RSiMe}_2\text{X}$ .



**Table 2.4A** Interaction between chlorodimethylsilylmethylpyrid-2-one (2.6A) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (2.6A) : NMI			
		1:0	1:0.5	1:1	0:1
$^1\text{H}$	H-2	-	9.2	8.8	7.4
	H-4	-	7.5	7.4	7.0
	H-5	-	7.3	7.2	6.9
	N-Me	-	4.1	4.0	3.7
	H-3	6.9	6.9	6.9	-
	H-4	7.9	8.1	8.2	-
	H-5	6.8	6.8	6.5	-
	H-6	7.7	7.9	7.9	-
	N-CH <sub>2</sub>	3.7	3.8	3.9	-
	SiMe	0.64	0.66	0.65	-
$^{13}\text{C}$	C-2	-	137.2	137.5	137.8
	C-4	-	122.5	124.5	129.5
	C-5	-	119.3	122.0	120.1
	N-Me	-	35.5	34.8	33.3
	C-2	160.1	162.9	162.8	-
	C-3	113.6	113.0	113.0	-
	C-4	139.3	139.4	139.5	-
	C-5	115.8	114.6	114.4	-
	C-6	143.3	144.0	144.1	-
	N-CH <sub>2</sub>	42.2	42.6	40.1	-
	SiMe	7.5	4.5	2.9	-
$^{29}\text{Si}$	SiMe	-41.1	-48.8 (sbr)	-54.2	-
Quantities used :					
2.6A (mmol)		2	2	2	-
NMI (mmol)		-	1	2	2
Solvent : CD <sub>3</sub> CN, 2.0 ml					

Table 2.5A Interaction between trichlorosilylmethylpyrid-2-one (2.8A) and  
N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (2.8A) : NMI			
		1:0	1:1	1:2	0:1
$^1\text{H}$	H-2	-	7.4	7.4	7.4
	H-4	-	7.2	7.2	7.0
	H-5	-	7.1	7.0	6.9
	N-Me	-	4.0	4.0	3.7
	H-3	7.1	7.2	7.2	-
	H-4	8.1	9.0	9.0	-
	H-5	7.0	7.3	7.3	-
	H-6	8.0	8.2	8.1	-
	N-CH <sub>2</sub>	4.0	3.8	3.8	-
$^{13}\text{C}$	C-2	-	136.0	136.2	137.7
	C-4	-	125.0	124.8	129.5
	C-5	-	121.8	121.0	120.1
	N-Me	-	35.5	35.4	33.3
	C-2	160.8	160.0	160.2	-
	C-3	114.0	114.7	114.5	-
	C-4	140.0	141.0	141.0	-
	C-5	115.4	116.0	116.0	-
	C-6	146.1	145.2	145.3	-
	N-CH <sub>2</sub>	44.2	55.0	55.1	-
$^{29}\text{Si}$	SiCl <sub>3</sub>	-77.7 (sbr)	-170.6 (sbr)	-171.1 (sbr)	-
Quantities used:					
2.8A (mmol)		2	2		-
NMI (mmol)		-	2		2
Solvent : CDCl <sub>3</sub> , 2.0 ml					

Table 2.6A Interaction between dichloromethylsilylmethylpyrid-2-one (2.7A) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (2.7A): NMI			
		1:0	1:1	1:2	0:1
$^1\text{H}$	H-2	--	9.4	8.7	7.4
	H-4	--	7.5	7.4	7.0
	H-5	--	7.3	7.3	6.9
	NMe	--	4.1	4.0	3.7
	H-3	7.0	7.7	7.5	--
	H-4	8.0	8.3	8.3	--
	H-5	6.8	7.2	6.9	--
	H-6	7.9	8.0	8.0	--
	NCH <sub>2</sub>	3.9	3.8	3.7	--
	SiMe	0.95	1.0	0.7 and 1.0	--
$^{13}\text{C}$	C-2	--	137.8	137.8	137.8
	C-4	--	122.8	123.1	129.5
	C-5	--	115.3	120.2	120.1
	NMe	--	35.6	32.9	33.3
	C-2	162.2	161.1	160.4 and 160.2	--
	C-3	113.9	114.1	112.0 and 113.0	--
	C-4	139.0	139.8	138.0 and 139.0	--
	C-5	114.5	115.3	114.0 and 117.0	--
	C-6	144.8	145.3	143.3 and 144.0	--
	NCH <sub>2</sub>	44.0	42.0	39.0 and 47.0	--
	SiMe	11.9	4.8	3.1 and 11.0	--
$^{29}\text{Si}$	SiMe	-52.5 (sbr)	-72.9	-73.0 and -160.5 (sbr)	--
Quantities used:					
(2.7A) (mmol)	2	2	2	--	--
NMI (mmol)	--	2	4	2	--
Solvent: CDCl <sub>3</sub> , 2.0 ml					

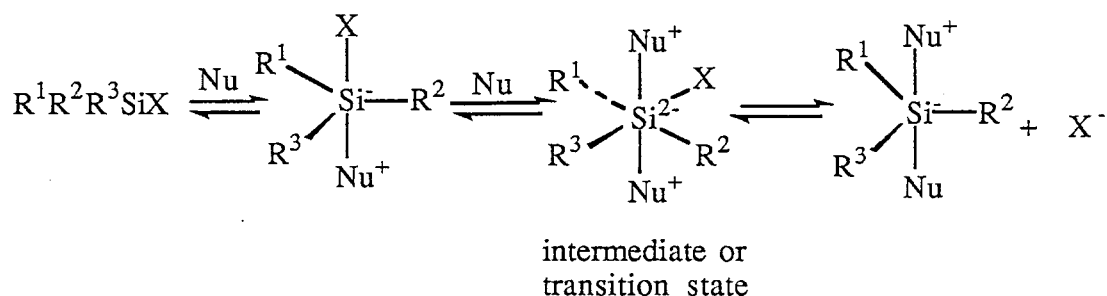


**SECTION B**

*A Map of Nucleophilic Substitution at Silicon in Solution*

## 2.1B INTRODUCTION:

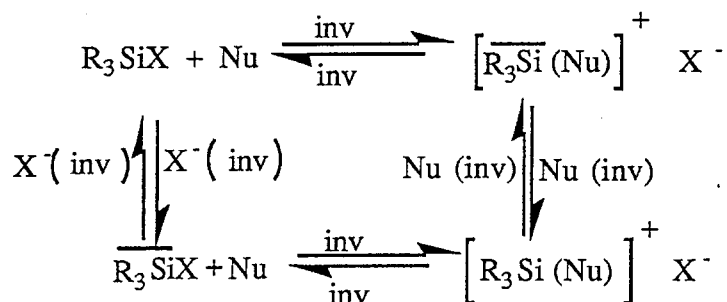
Reactions of trimethylhalosilanes with Lewis bases have been frequently investigated in order to gain information on donor-acceptor properties and the structure of the products. Additional interest has recently been shown in investigation of the question of the role of added nucleophiles in the racemization of chiral organosilanes and the nucleophilic substitution at silicon<sup>7b,8,39,78,122-125</sup>. Three mechanisms have been proposed for nucleophilically-activated racemization and solvolysis of halosilanes. One mechanism involves expansion of coordination at silicon, involving ultimately hexacoordinated intermediate species (Scheme 2.1B)<sup>7b</sup>, while another involves intermediate tetracoordinate ionic silicon



Scheme 2.1B

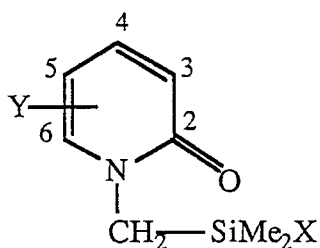
species with ionisation of the Si-halogen bond<sup>8</sup>. Recently, an alternative pathway for nucleophile-assisted racemization of halosilanes involving halide exchange has been suggested which led to an extension of the second mechanism as shown in Scheme 2.2B<sup>9</sup>. In spite of many studies in this field no clear distinction between the first two mechanisms can yet be made and so the mechanism of nucleophilic

substitution at silicon is still controversial and an area of active current research<sup>4,5</sup>. In the previous section we have described the development of a model



Scheme 2.2B

for mapping of nucleophilic substitution at silicon in solution. In this section we are going to describe how the method has been applied successfully for the mapping of simple S<sub>N</sub>2 nucleophilic substitution on a series of compounds of the type (2.1B) with different leaving groups and substituents on the ring on the basis of <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR data.



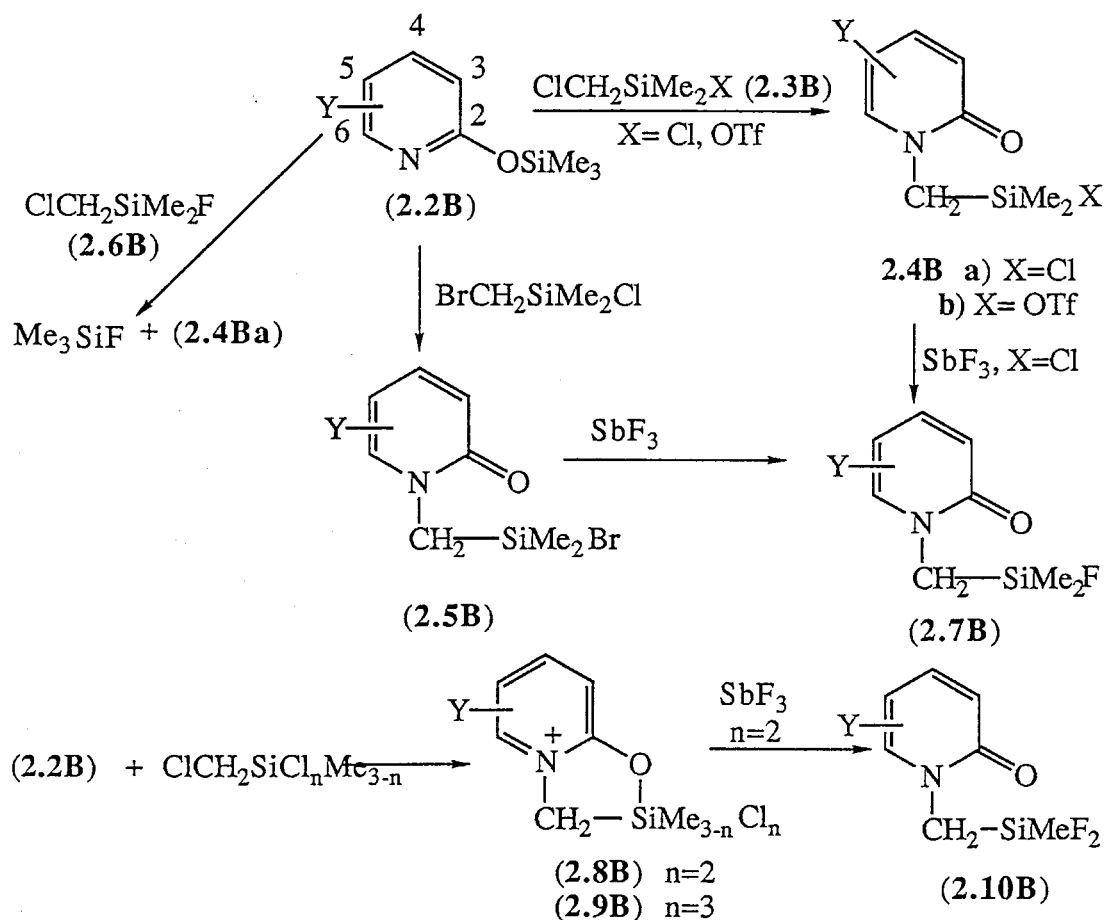
(2.1B) X= OR, F, Cl, Br, CF<sub>3</sub>SO<sub>3</sub>

Y= H, 3-NO<sub>2</sub>, 3-OMe, 5-Cl, 6-Cl, 6-Me

## 2.2B RESULTS AND DISCUSSION:

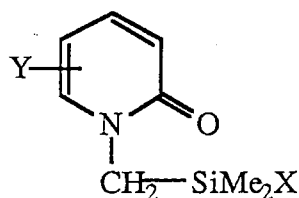
When 2-trimethylsiloxypyridine (2.2B) was treated with chloromethyldimethyl-

silane (2.3B), 2-pyridone derivatives (2.4B, X= Cl, OTf) were obtained, with liberation of one equivalent of chlorotrimethylsilane as shown in Scheme 2.3B. The bromoderivatives (2.5B) were prepared by treating (2.2B) with bromomethyldimethylchlorosilane (Scheme 2.3B). We found that when (2.2B) was treated with chloromethyldimethylfluorosilane (2.6B) it gives chloro derivatives (2.4Ba) and trimethylfluorosilane. So the fluoro (2.7B) derivatives were prepared by treating either the bromo (2.5B) or chloro derivatives (2.4Ba) with antimony trifluoride (Scheme 2.3B). Similarly we have prepared dichloro(2.8B), trichloro(2.9B) and difluoro (2.10B) pyridone derivatives (Scheme 2.3B)

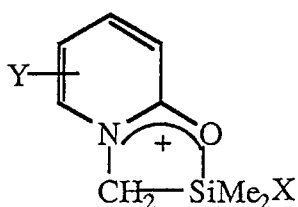


Scheme 2.3B

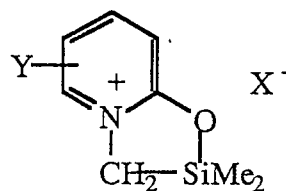
The mapping method involved the determination of the positions of a particular compound on the reaction continuum, **2.11B**, **2.12B**, **2.13B** by analysing the  $^{13}\text{C}$  (or  $^1\text{H}$ ) NMR chemical shifts of the pyridone ring and comparing them with model compounds for the extremes **2.11B** and **2.13B**.



(2.11B)

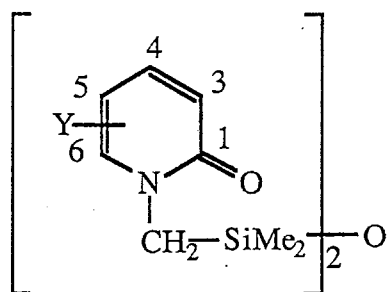


(2.12B)



(2.13B)

We chose disiloxane (**2.14B**) whose  $^{29}\text{Si}$  chemical shifts show that it is purely tetracoordinate as our model for our study. The model for (**2.13B**) was then prepared by silylation of (**2.14B**) with trimethylsilyl triflate. Tables 2.1B-2.6B show the carbon-13 chemical shifts changes during titration of disiloxane (**2.14B**; SiO) with successive amounts of trimethylsilyl triflate to obtain (**2.15B**; SiO+) (Tables 2.1B-2.6B)



(2.14B) Y=H

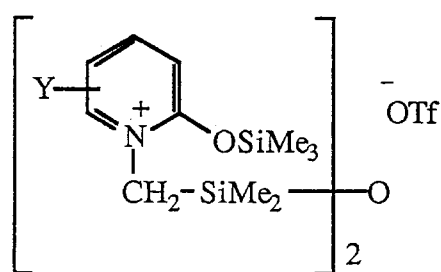
=3-OMe

=3-NO<sub>2</sub>

=6-Me

=5-Cl

=6-Cl



(2.15B) Y=H

=3-OMe

=3-NO<sub>2</sub>

=6-Me

=5-Cl

=6-Cl

**Table 2.1B** Interaction between disiloxane (2.14B, Y=H) and trimethylsilyl triflate (Me<sub>3</sub>SiOTf) : NMR Data

$\delta$ (ppm)		Ratio of (2.14B, Y=H): Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-3	6.4	7.6	7.5
	H-4	7.2	8.3	8.2
	H-5	6.0	7.2	7.2
	H-6	7.1	8.1	8.0
	NCH <sub>2</sub>	3.4	4.0	4.0
	SiMe	0.16	0.21	0.21
<sup>13</sup> C	C-2	162.2	162.5	162.5
	C-3	119.7	117.8	118.1
	C-4	138.3	141.5	141.6
	C-5	105.6	115.0	115.1
	C-6	138.6	146.9	147.1
	CF <sub>3</sub>	--	119.0	119.0
	<sup>1</sup> J <sub>CF</sub>	--	317.0 Hz	317.1 Hz
	NCH <sub>2</sub>	42.4	42.5	42.5
	SiMe	0.63	0.40	0.40
<sup>29</sup> Si	SiMe	4.2	nr	2.5
Quantities used:				
(2.14B, Y=H) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		--	2	8
Solvent : CDCl <sub>3</sub> , 2.0 ml				

**Table 2.2B** Interaction between disiloxane (**2.14B**, Y= 3-OMe) and trimethylsilyl triflate (Me<sub>3</sub>SiOTf) : NMR Data

$\delta$ (ppm)		Ratio of ( <b>2.14B</b> , Y=3-OMe) : Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-4	6.9	7.7	7.7
	H-5	6.1	7.2	7.2
	H-6	6.6	7.5	7.5
	OMe	3.8	4.0	4.0
	NCH <sub>2</sub>	3.6	4.0	4.0
	SiMe	0.20	0.20	0.19
<sup>13</sup> C	C-2	157.8	156.0	156.0
	C-3	112.2	122.7	123.1
	C-4	149.7	146.6	146.8
	C-5	105.1	116.6	116.9
	C-6	129.3	130.8	130.9
	OMe	55.8	57.2	57.2
	CF <sub>3</sub>	- -	119.5	119.0
	<sup>1</sup> J <sub>CF</sub>	- -	318.4Hz	317.1 Hz
	NCH <sub>2</sub>	42.7	42.8	42.9
	SiMe	0.40	0.98	0.75
<sup>29</sup> Si	SiMe	3.4	nr	9.5
Quantities used :				
(2.14B, Y=3-OMe) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		- -	2	8
Solvent : CDCl <sub>3</sub> , 2.0 ml				

**Table 2.3B** Interaction between disiloxane (2.14B, Y= 5-Cl) and trimethylsilyl-triflate (Me<sub>3</sub>SiOTf) : NMR Data

$\delta$ (ppm)		Ratio of (2.14B, Y= 5-Cl) : Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-3	6.2	7.1	7.1
	H-4	7.2	8.2	8.2
	H-6	6.5	8.0	8.0
	NCH <sub>2</sub>	3.8	4.1	4.1
	SiMe	0.20	0.10	0.10
<sup>13</sup> C	C-2	160.9	161.6	161.7
	C-3	120.5	123.5	123.9
	C-4	139.9	146.4	146.7
	C-5	112.4	115.5	115.7
	C-6	136.0	139.0	139.2
	CF <sub>3</sub>	- -	119.0	119.0
	<sup>1</sup> J <sub>CF</sub>		318.0 Hz	317.1 Hz
	NCH <sub>2</sub>	43.1	42.9	43.0
	SiMe	0.51	0.80	0.63
<sup>29</sup> Si	SiMe	3.5 (sbr)	nr	7.2 (sbr)
Quantities used :				
(2.14B, Y= 5-Cl) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		- -	2	8
Solvent : CDCl <sub>3</sub> , 2.0 ml				



Table 2.4B Interaction between disiloxane (2.14B, Y= 6-Cl) and trimethylsilyl triflate (Me<sub>3</sub>SiOTf) : NMR Data

d (ppm)		Ratio of (2.14B, Y= 6-Cl) : Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-3	6.5	7.3	7.4
	H-4	7.2	8.1	8.1
	H-5	6.4	7.1	7.2
	NCH <sub>2</sub>	3.8	3.9	3.9
	SiMe	0.20	0.10	0.17
<sup>13</sup> C	C-2	162.8	161.0	163.5
	C-3	117.0	116.3	117.4
	C-4	137.9	145.8	146.4
	C-5	106.9	113.3	112.3
	C-6	137.9	141.8	142.5
	CF <sub>3</sub>	--	119.0	118.9
	<sup>1</sup> J <sub>CF</sub>	--	318.0 Hz	317.0 Hz
	NCH <sub>2</sub>	39.8	41.5	41.4
	SiMe	0.92	1.61	--
<sup>29</sup> Si	SiMe	3.5 (sbr)	nr	7.2 (sbr)
Quantities used :				
(2.14B, Y= 6-Cl) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		--	2	8
Solvent : CDCl <sub>3</sub> +CD <sub>3</sub> CN (1:1), 2.0 ml				

**Table 2.5B** Interaction between disiloxane (2.14B, Y= 3-NO<sub>2</sub>) and trimethylsilyl triflate (Me<sub>3</sub>SiOTf) : NMR Data

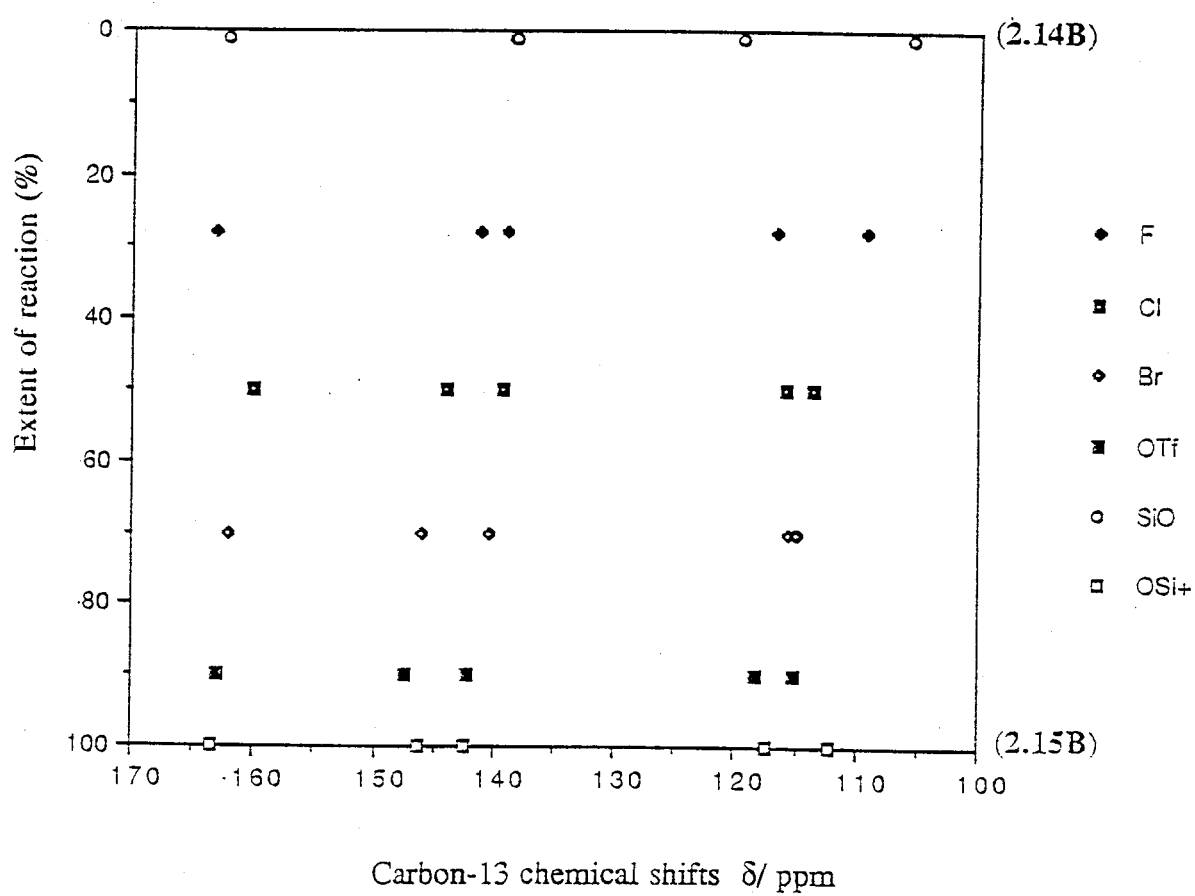
$\delta$ (ppm)		Ratio of (2.14B, Y= 3-NO <sub>2</sub> ) : Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-4	8.3	8.8	8.8
	H-5	6.3	7.2	7.2
	H-6	8.0	8.5	8.5
	NCH <sub>2</sub>	3.7	3.9	4.0
	SiMe	0.15	0.10	0.10
<sup>13</sup> C	C-2	154.9	158.1	158.2
	C-3	138.2	135.8	135.0
	C-4	146.1	146.9	147.0
	C-5	103.7	114.3	114.6
	C-6	138.2	142.4	142.5
	CF <sub>3</sub>	--	120.0	119.4
	<sup>1</sup> J <sub>CF</sub>	--	318.4 Hz	317.1 Hz
	NCH <sub>2</sub>	44.5	42.4	42.5
	SiMe	0.57	--	--
<sup>29</sup> Si	SiMe	5.0	nr	2.6
Quantities used:				
(2.14B, Y= 3-NO <sub>2</sub> ) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		--	2	8
Solvent : CD <sub>2</sub> Cl <sub>2</sub> +CD <sub>3</sub> CN, (1:1), 2.0 ml				

Table 2.6B Interaction between disiloxane (**2.14B**, Y= 6-Me) and trimethylsilyl  
triflate (Me<sub>3</sub>SiOTf) : NMR Data

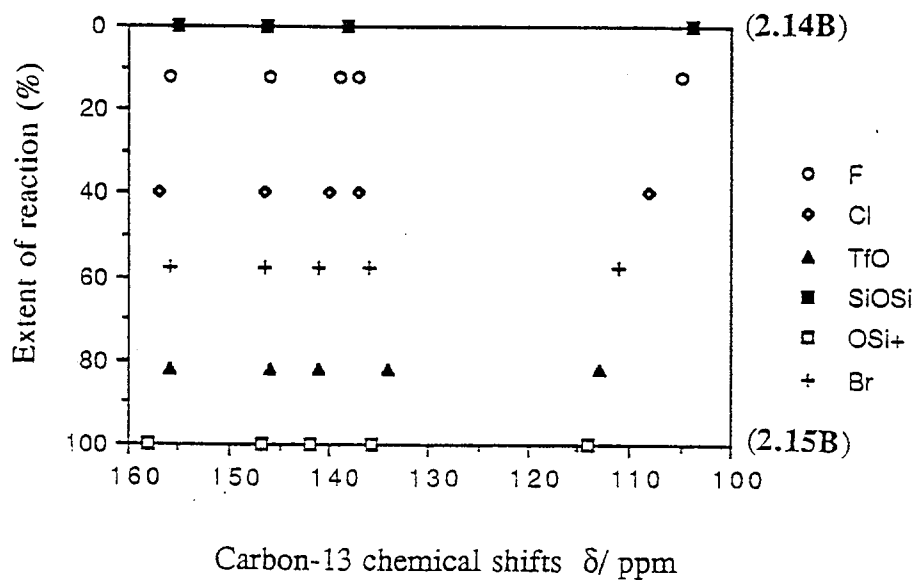
$\delta$ (ppm)		Ratio of ( <b>2.14B</b> , Y= 6-Me) : Me <sub>3</sub> SiOTf		
		1:0	1:1	1:4
<sup>1</sup> H	H-3	6.6	7.2	7.2
	H-4	7.4	7.9	8.0
	H-5	6.3	7.0	7.0
	Me	2.5	2.7	2.6
	NCH <sub>2</sub>	3.5	3.8	3.8
	SiMe	0.29	0.20	0.32
<sup>13</sup> C	C-2	163.2	162.7	163.8
	C-3	114.2	116.9	119.5
	C-4	147.5	151.3	153.9
	C-5	109.6	111.6	112.4
	C-6	139.9	145.1	147.4
	CF <sub>3</sub>	--	119.0	118.1
	<sup>1</sup> J <sub>CF</sub>	--	318.1 Hz	317.0 Hz
	Me	21.4	20.8	21.3
	NCH <sub>2</sub>	38.2	39.9	40.8
	SiMe	2.2	2.0	--
<sup>29</sup> Si	SiMe	4.2	nr	7.4 (sbr)
Quantities used :				
(2.14B, Y= 6-Me) (mmol)		2	2	2
Me <sub>3</sub> SiOTf (mmol)		--	2	8
Solvent : CDCl <sub>3</sub> , 2ml				

Figure 2.1B shows the variation of the extent of reaction (i.e., the extent of Si-O bond formation) for the unsubstituted pyridones **2.1B** ( $Y = H$ ,  $X = F, Cl, Br, CF_3SO_3$ ). The extent of reaction followed the expected order<sup>4,5</sup> with the leaving group ability falling in the order  $OTf > Br > Cl > F$ . Figures 2.2B and 2.3B shows the same effect, but for 3-NO<sub>2</sub> and 6-Me substituted pyridones respectively. In each case the zero and 100% reactions refer to the appropriate (**2.14B**) and its silylated derivative (**2.15B**). The same general trend in leaving group ability was followed in both cases, but the relative extent of reaction was modified by the substituent. With the strongly electron-withdrawing 3-NO<sub>2</sub> group the extent of reaction for each leaving group was significantly less than for the unsubstituted series. Conversely, the reactions were more advanced for the electron donating 6-Me series. For example, the extent of reaction for fluorides was 12% for 3-NO<sub>2</sub>; 30% for H and 45% for 6-Me; for the chlorides 40%, 3-NO<sub>2</sub>; 50%, H and about 70%, 6-Me. The Si-O bond in 3-NO<sub>2</sub> substituted silyl triflate was only 80% formed, whereas for the H and 6-Me derivatives it was around 90% formed. The extent of reaction in the case of 6-Cl, 5-Cl, and 3-OMe are shown in figures 2.4B-2.6B. We found that in the case of fluorosilyl pyridones the substituent effect decreases in the order 6-Me > 6-Cl > H > 5-Cl > 3-OMe > 3-NO<sub>2</sub> and in the chloride series the order was 6-Me > 5-Cl > 6-Cl  $\approx$  H > 3-OMe > 3-NO<sub>2</sub>. The spectra of the fluoride series were obtained both in CDCl<sub>3</sub> and CD<sub>3</sub>CN and there was almost no difference in chemical shifts between the spectra in different solvents. But there was a problem with solubility in the bromide series and a variety of solvents including methanol was used. Although solvent was not an important factor in determining the extent of reaction in the fluoro series it may be in others. So variations in solvent made direct comparison difficult between two differently substituted bromides.

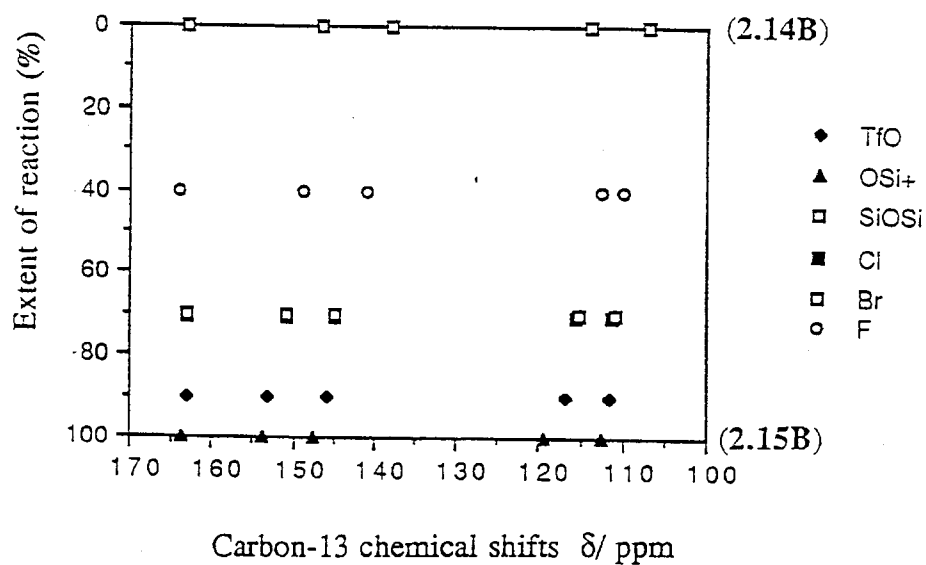
Figure 2.1B Variation of C-13 chemical shifts with extent of reaction for unsubstituted silylpyridones (2.1B, Y=H)



**Figure 2.2B** Variation of C-13 chemical shifts with extent of reaction for 3-NO<sub>2</sub> silylpyridones (2.1B, Y=3-NO<sub>2</sub>)



**Figure 2.3B** Variation of C-13 chemical shifts with extent of reaction for 6-Me silylpyridones (2.1B, Y=6-Me)



**Figure 2.4B** Variation of C-13 chemical shifts with extent of reaction for  
6-Cl silylpyridones (**2.1B**, Y=6-Cl)

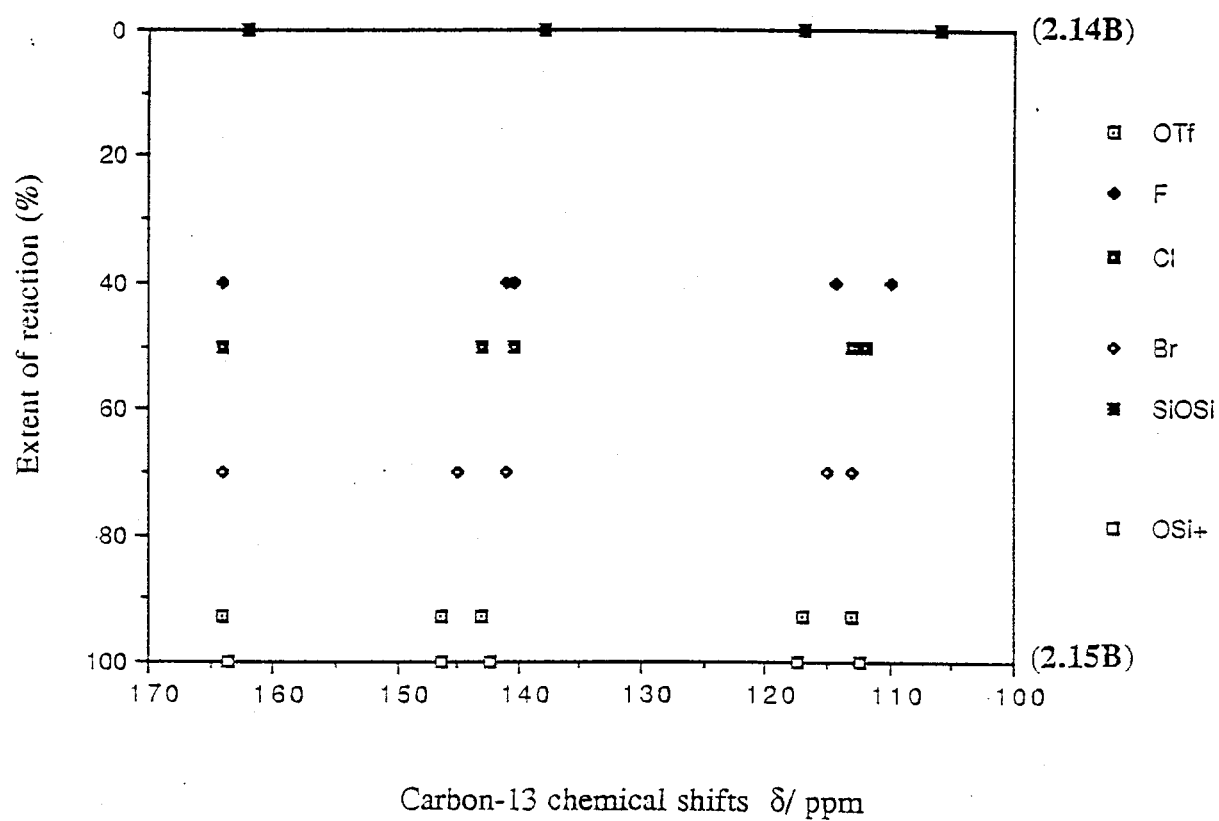


Figure 2.5B Variation of C-13 chemical shifts with extent of reaction for  
5-Cl silylpyridones (2.1B, Y=5-Cl)

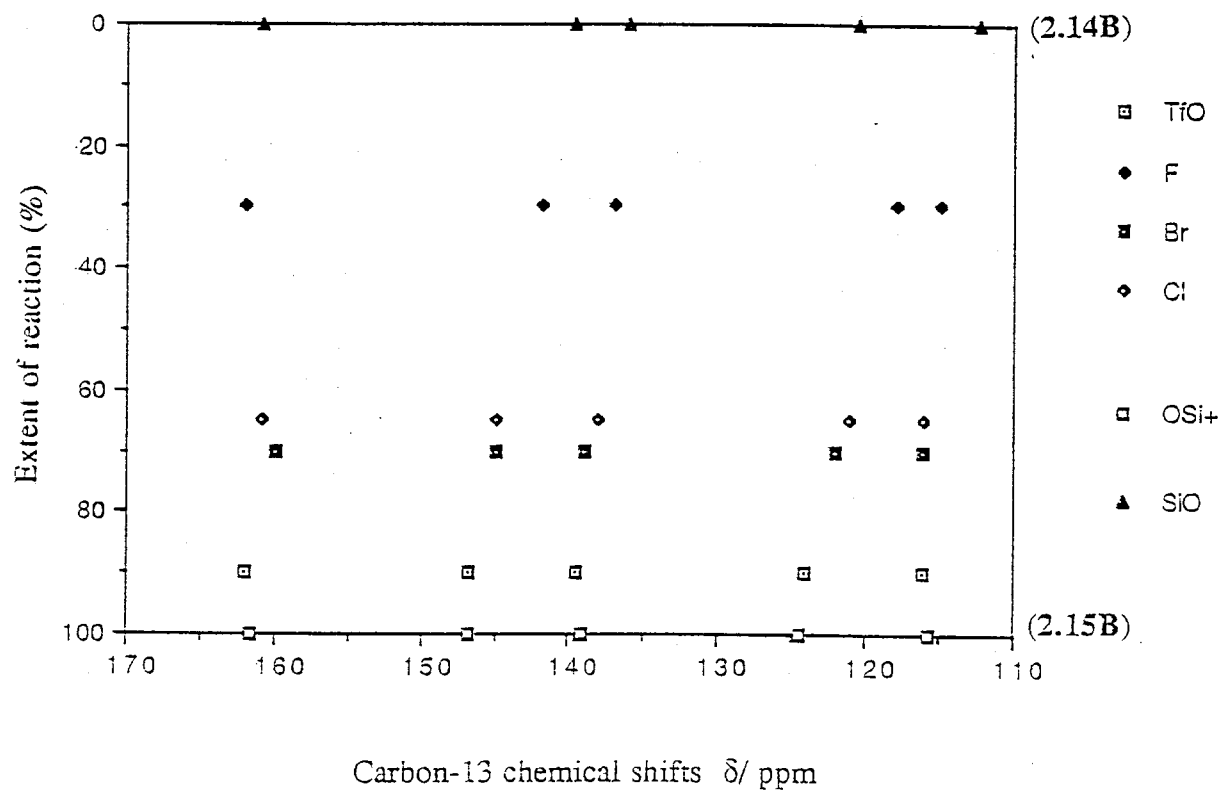
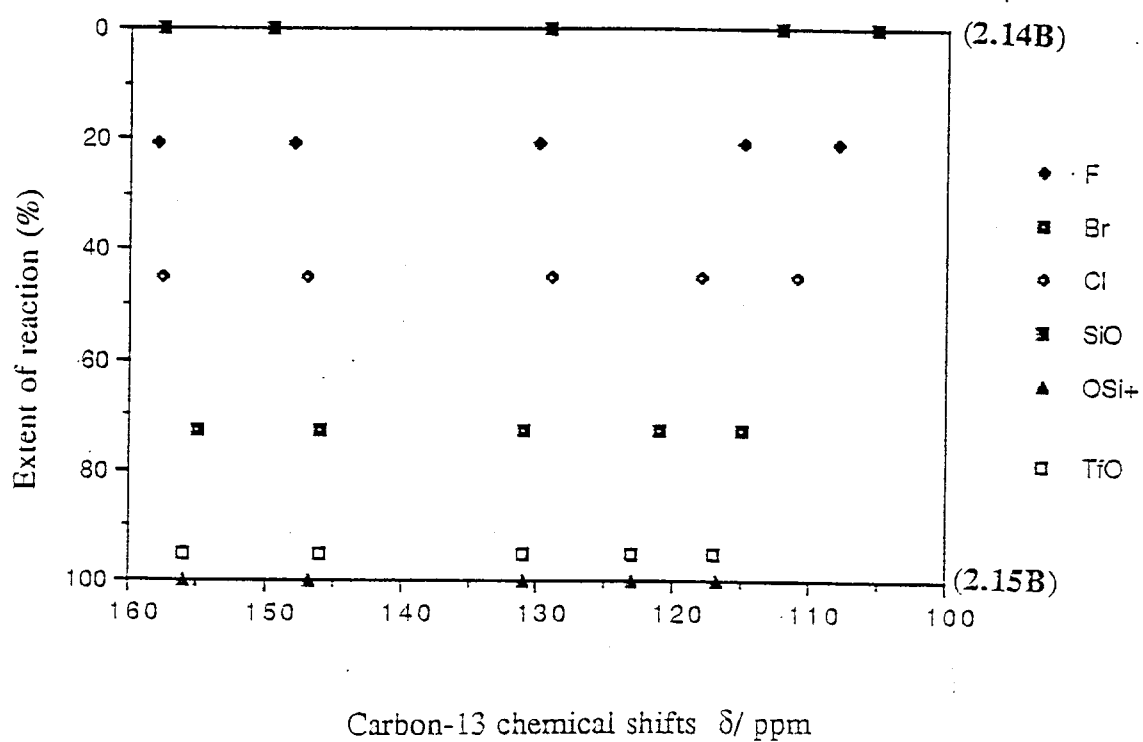
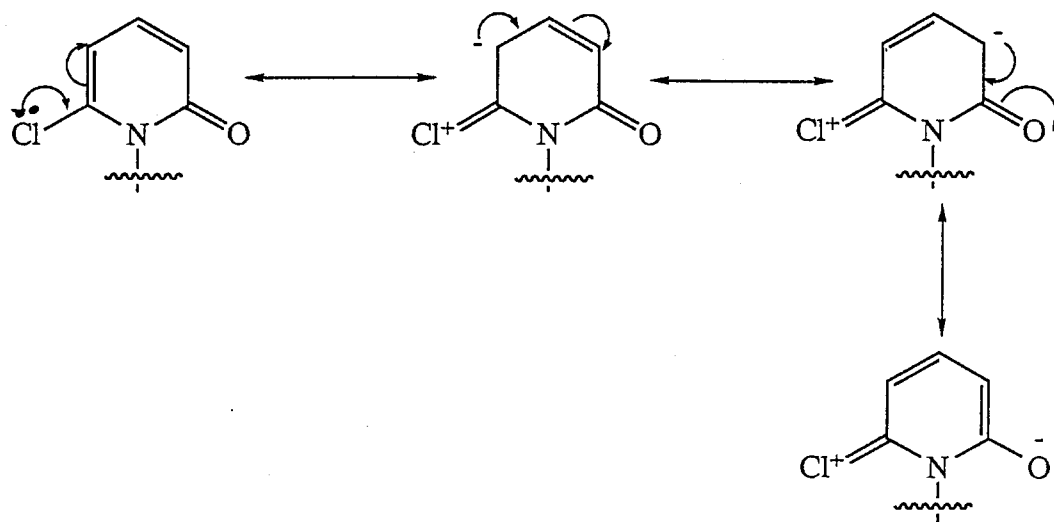




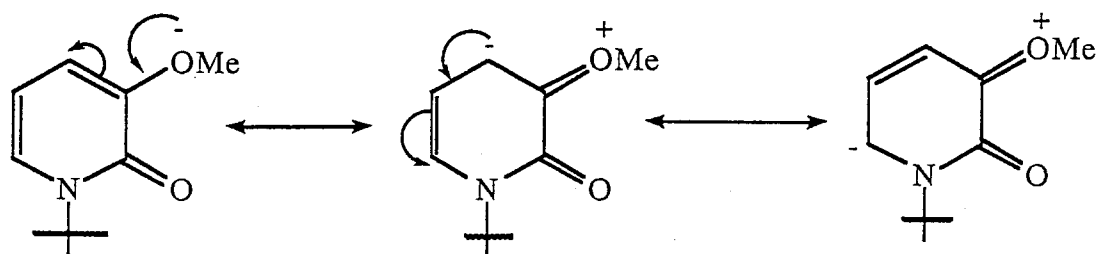
Figure 2.6B Variation of C-13 chemical shifts with extent of reaction for 3-OMe silylpyridones (2.1B, Y=3-OMe)



The 6-Cl substituent in **2.1B** is electron supplying by the resonance effect, which particularly pronounced in the 6-position. It increases the nucleophilicity at oxygen as shown in Scheme 2.4B and hence the extent of reaction also increase accordingly. On the other hand the 3-OMe group is electron withdrawing by the



Scheme 2.4B

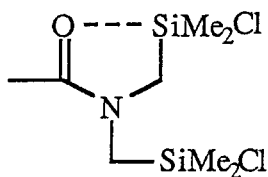


Scheme 2.5B

inductive effect which decreases the nucleophilicity at oxygen and hence the extent of Si-O bond formation decreases. Scheme 2.5B shows that the resonance electron supply of the OMe group cannot affect the C=O bond in the way that occurs with the 6-Cl substituent.

The question arises as the nature of the species being studied. There could be two possible explanations. Either there is a continuum of structures as the Si-X bond extends and the O-Si bond forms, or there is an equilibrium between  $2.11\text{B} \rightleftharpoons 2.12\text{B}$  and  $2.12\text{B} \rightleftharpoons 2.13\text{B}$  which in view of the single sets of resonances in NMR spectra of each nucleus, must involve rapid exchange on the NMR time scale. X-ray structural analysis<sup>76</sup> on chelated pentacoordinate silyl amides showed that the Si-Cl bond length increases as the O-Si bond length decreases. It is reasonable to assume that the solutions structures could be similarly hybrid. But we do not have any definitive evidence to support this hypothesis. If there would have been an equilibrium, then the solution of bromosilyl pyridones would have been approximately 50%  $2.13\text{B}$ , but conductivity study has shown that it was non ionic. So, there could be a continuum of structures rather than equilibrium. But a slightly broadened peak in silicon-29 NMR observed for  $2.5\text{B}$ , (X=H) could not be explained in terms of continuum structures but it could be an effect of the quadrupolar bromine. Triflate derivatives were found to be ionic and showed high conductivity. A continuum of structures appears to be more appropriate than equilibria between  $2.11\text{B} \rightleftharpoons 2.12\text{B}$  or  $2.12\text{B} \rightleftharpoons 2.13\text{B}$ .

In order to map completely the progress of the reaction it was necessary to correlate the Si-O bond formation with the coordination state of silicon. The X-ray crystal structure of ( $2.16\text{B}$ ) has been reported<sup>58</sup> and found that the one silicon atom is completely pentacoordinate<sup>58,70</sup>. We measured the silicon-29 NMR chemical shifts in  $\text{CDCl}_3$  and found that the pentacoordinate silicon atom has a resonance at -39.9 ppm and the four coordinate silicon atom appears at 26.8 ppm. The silicon-29 NMR chemical shifts of the unsubstituted and 6-Cl substituted

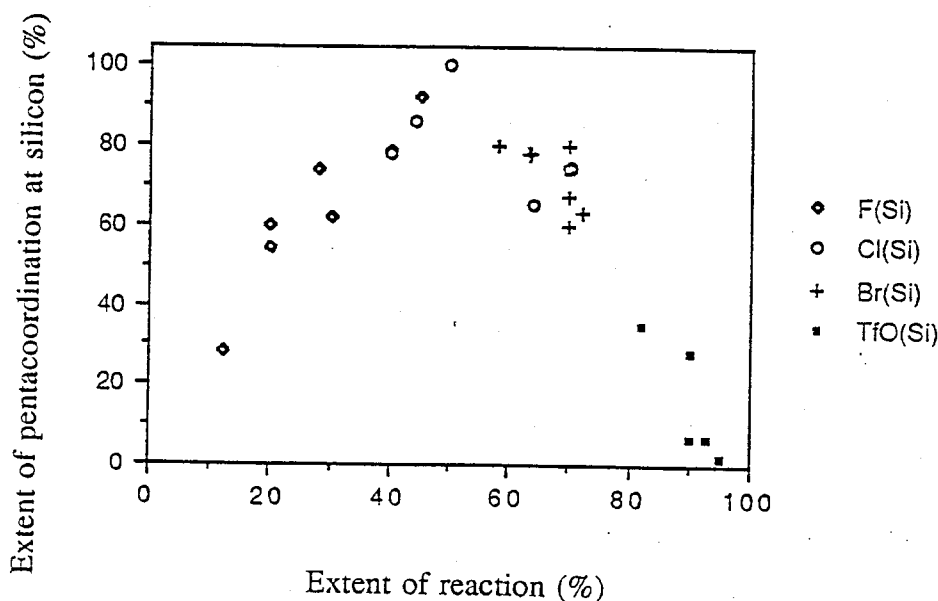


(2.16B)

chlorosilane, **2.1B** both appeared at -41 ppm and their extent of reaction measured by carbon-13 NMR, were both 50%. The maximum extent of pentacoordination was observed in 6-Cl substituted chlorosilanes (**2.1B**). The 'extent of reaction' was least advanced with the electron withdrawing 3-OMe group, then proceeds to a fully pentacoordinate intermediate with H and 6-Cl substituents, and then O-Si bond formation advanced significantly with the 6-Me substituent with ultimate weakening of the Si-Cl bond. We used these results to estimate the 'extent of pentacoordination' at silicon. The silicon-29 chemical shifts of Me<sub>3</sub>SiF, Me<sub>3</sub>SiCl, Me<sub>3</sub>SiBr and the tetracoordinate silicon in **2.16B** all appear within  $\pm 2$  ppm of +28 ppm, which was used as the limiting value for 0% coordination. The assumption was that -40 ppm represents complete pentacoordination for all derivatives F, Cl, and Br. This was reasonable in view of the chemical shift of both the 6-Me substituted fluorosilanes, **2.1B**, with  $\delta^{29}\text{Si}$  -35 ppm and 40% reaction from <sup>13</sup>C NMR data, and  $\delta^{29}\text{Si}$  -27 ppm for the 3-NO<sub>2</sub> substituted bromosilane, **2.1B**, with an extent of reaction about 60% from carbon-13 NMR data. A silicon-29 NMR chemical shift of, say -4 ppm was taken as the mean value of the two extremes, **2.11B** and **2.12B**, and represented 50% pentacoordination while -40 ppm represented 100% pentacoordination. The limiting value of the silicon-29 NMR chemical shift of **2.13B** was taken to be +40 ppm from the chemical shift of O-trimethylsilylated-N-methyl pyridone. For species on the **2.12B**, **2.13B**

manifold the silicon-29 NMR chemical shift range was assumed to be -40 ppm and +40 ppm, and the extent of pentacoordination for intermediate species was readily obtained. For example, the silicon-29 chemical shift of unsubstituted silyl fluoride (2.7B, Y=H) was -22.3 ppm (with Si-F coupling constant 256.8 Hz). So the extent of pentacoordination was about 60%. The silicon-29 chemical shift of unsubstituted silyl chloride (2.4Ba, Y=H) was -41.1 ppm and hence the extent of pentacoordination was 100%. Similarly the silicon-29 chemical shifts for bromide (2.5B, Y=H) and triflate (2.4Bb, Y=H) derivatives were -18.4 and 32.3 ppm respectively. The respective extents of pentacoordination were 70% and 5%. For the whole series of compounds, 2.1B, the extent of pentacoordination at silicon was calculated as describe above, and correlated with the extent of reaction as determined by carbon-13 chemical shifts. Figure 2.7B shows the complete mapping of substitution at 2.1B. The Figure shows that the extent of reaction increases

Figure 2.7B Mapping of nucleophilic substitution at silicon

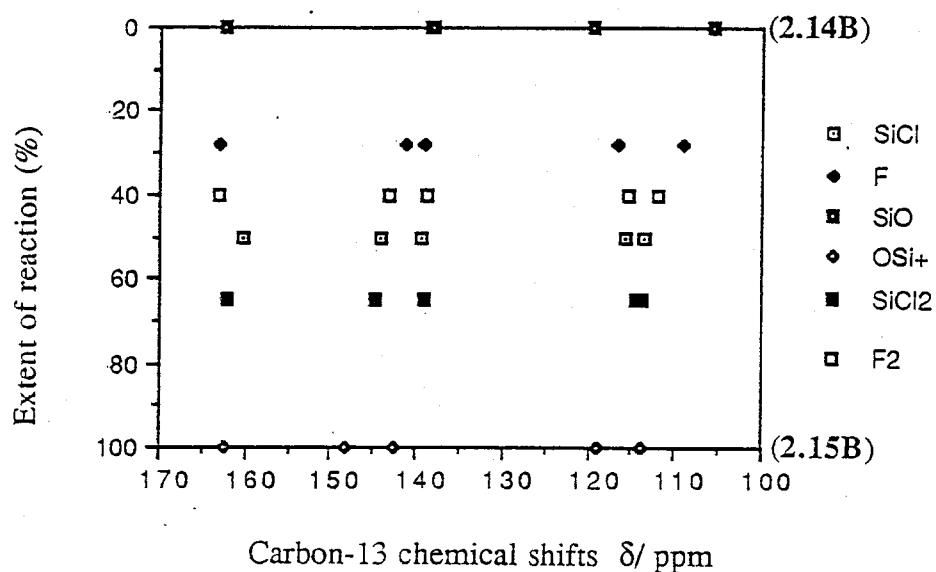


gradually when the leaving group changes from  $F \rightarrow Cl \rightarrow Br \rightarrow OTf$ . The extent of pentacoordination increases with the increase of extent of reaction and it was maximum at a certain point and then decreases again to almost 0%. We observed that the extent of pentacoordination was highest (about 100%) when the extent of reaction was about 50%. The approach to the pentacoordinated intermediate was characterised by the fluorosilanes, which were the least powerful leaving groups; the chlorides were clustered around the pentacoordinate intermediate position; the bromides all have about 70% reaction, and finally the triflates, which are excellent leaving groups, were almost fully reacted. The reaction therefore proceeds through a genuine pentacoordinate intermediate as was confirmed by silicon-29 NMR chemical shifts.

It is well established that the tendency to five coordination increases in the order  $R_3SiCl < R_2SiCl_2 < RSiCl_3$ <sup>68</sup>. We observed similar results with our silyl pyridones. For example, the unsubstituted difluoride (**2.10B**) and chloride (**2.8B**) silyl pyridones found to be more five coordinate compared to their respective monofluoride (**2.7B**) and chloride (**2.4Ba**). The extent of reactions are also greater for the dihalosilyl pyridones compared to monohalosilyl pyridones and the results are shown in Figure 2.8B. Similar results were obtained for 3-OMe, 5-Cl, and 6-Cl derivatives and the results are shown in Figures 2.9B-2.11B.

The effects of temperature on some of our new compounds have revealed interesting facts, especially in the case of fluoro (**2.7B**) and bromosilyl pyridones (**2.5B**). The silicon-29 NMR spectrum of (**2.7B**) and (**2.5B**) showed changes between  $-60^\circ$  and  $+60^\circ C$ . The proton and carbon-13 positions were relatively temperature independent. The silicon-29 NMR showed that the silicon atom of fluoro and bromo pyridones becomes more five coordinate at low temperature and

**Figure 2.8B** Comparison of carbon-13 chemical shifts of unsubstituted difluoro (2.10B) and chloro (2.8B) silyl pyridones with their respective monofluoro (2.7B) and chloro (2.4Ba) silyl pyridones.



**Figure 2.9B** Comparison of carbon-13 chemical shifts of 3-OMe difluoro (2.10B) and chloro (2.8B) silyl pyridones with their respective monofluoro (2.7B) and chloro (2.4Ba) silyl pyridones.

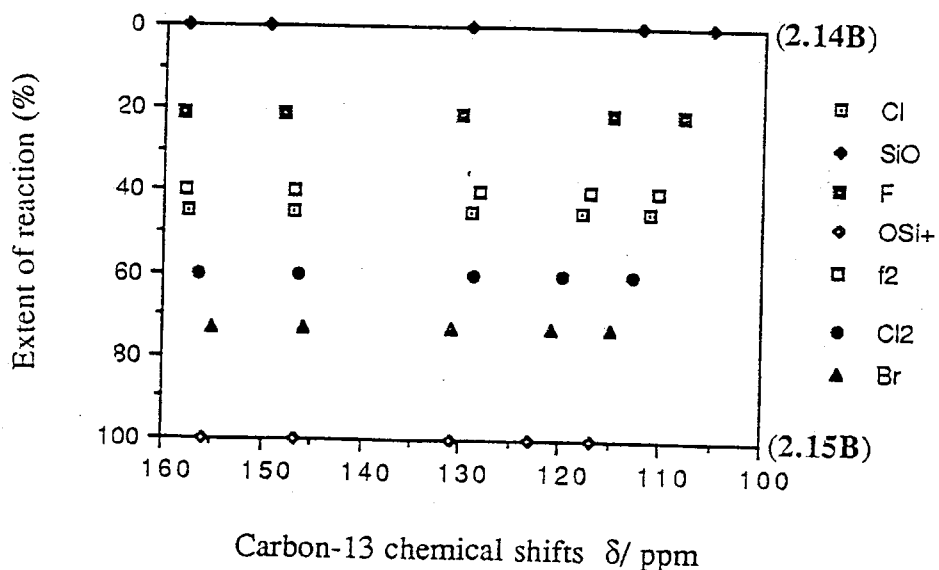


Figure 2.10B Comparison of carbon-13 chemical shifts of 5-Cl difluoro

(2.10B) and chloro (2.8B) silyl pyridones with their respective monofluoro (2.7B) and chloro (2.4Ba) silyl pyridones.

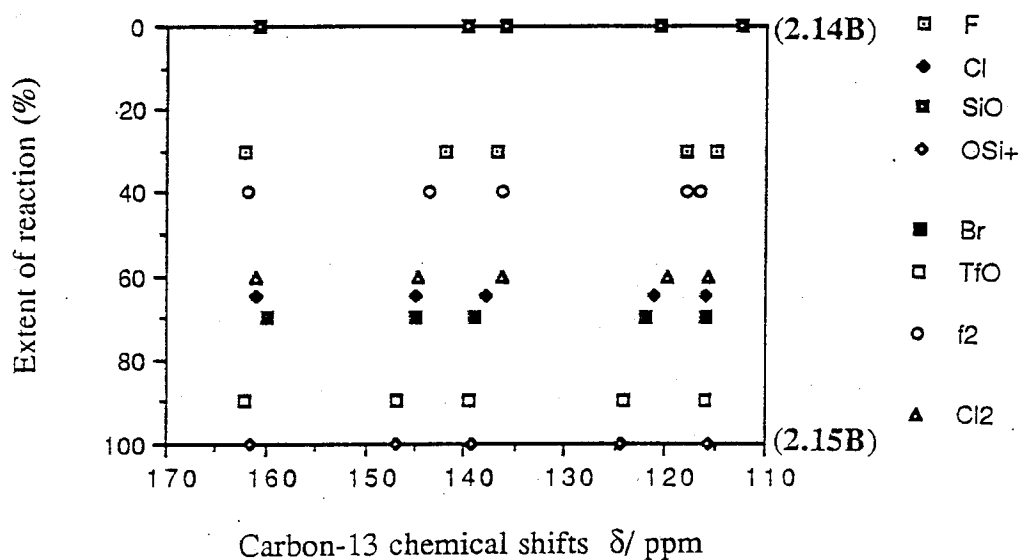
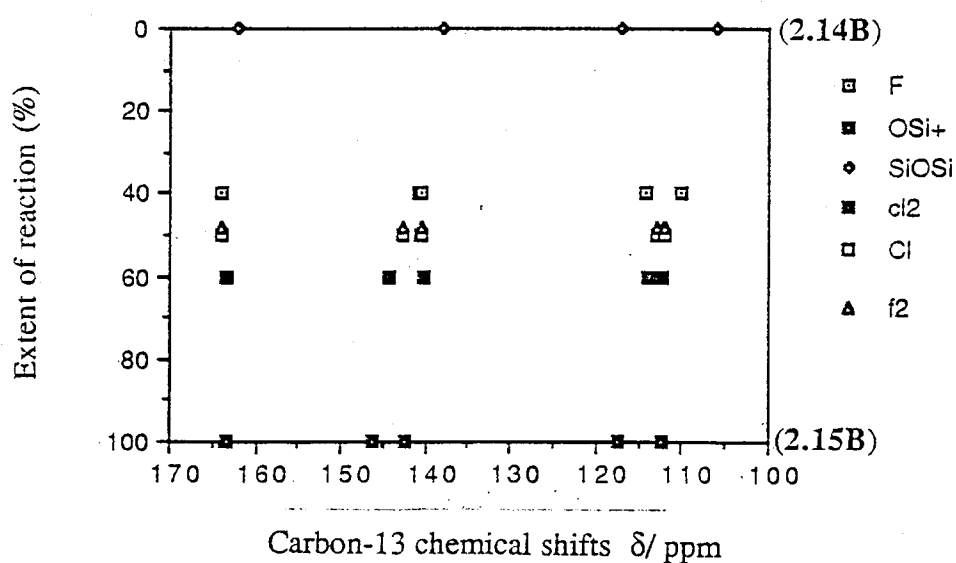


Figure 2.11B Comparison of carbon-13 chemical shifts of 6-Cl difluoro

(2.10B) and chloro (2.8B) silyl pyridones with their respective monofluoro (2.7B) and chloro (2.4Ba) silyl pyridones.

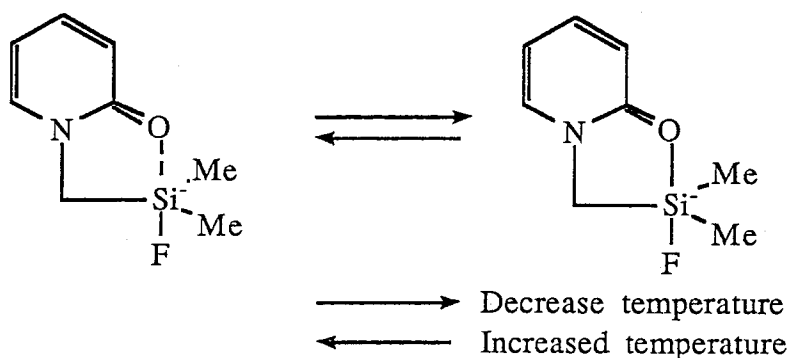




**Table 2.7B**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR chemical shifts ( $\delta$ / ppm) of fluorodimethylsilylmethylpyrid-2-one (**2.7B**, Y=H) at various temperatures.

Compound	Temp. (°C)	NMR Data	
(2.7B, Y=H)	RT	$^1\text{H}$	0.32 (d, $^3J_{\text{HSiF}}=6.8$ Hz, 6H, SiMe <sub>2</sub> ), 3.2 (s, 2H, NCH <sub>2</sub> ), 6.5-7.7 (m, 4H, arom)
		$^{13}\text{C}$	1.8 (d, $^2J_{\text{CSiF}}=25.0$ Hz, SiMe), 39.5 (d, $^2J_{\text{CSiF}}=44.0$ Hz, SiCH <sub>2</sub> ), 109.0, 116.8, 139.1, 141.4, 163.2
		$^{29}\text{Si}$	-22.3 (d, $^1J_{\text{SiF}}=256.8$ Hz)
	+54	$^1\text{H}$	0.31 (d, $^3J_{\text{HSiF}}=6.8$ Hz, 6H, SiMe <sub>2</sub> ), 3.2 (d, 2H, NCH <sub>2</sub> ), 6.5-7.6 (m, 4H, arom)
		$^{13}\text{C}$	1.5 (d, $^2J_{\text{CSiF}}=25.0$ Hz, SiMe), 40.0 (d, $^2J_{\text{CSiF}}=37.6$ Hz, SiCH <sub>2</sub> ), 108.9, 117.1, 139.1, 141.3, 163.3
		$^{29}\text{Si}$	-19.1 (d, $^1J_{\text{SiF}}=255.9$ Hz)
	-60	$^1\text{H}$	0.31 (d, $^3J_{\text{HSiF}}=6.5$ Hz, 6H, SiMe <sub>2</sub> ), 3.2 (s, 2H, NCH <sub>2</sub> ), 6.6-7.8 (m, 4H, arom)
		$^{13}\text{C}$	2.3 (d, $^2J_{\text{CSiF}}=25.9$ Hz, SiMe), 38.6 (d, $^2J_{\text{CSiF}}=47.9$ Hz, SiCH <sub>2</sub> ), 110.0, 116.0, 139.0, 142.0, 162.0
		$^{29}\text{Si}$	-30.4 (d, $^1J_{\text{SiF}}=253.0$ Hz)

four coordinate at high temperature. The chloro (**2.4Ba**) and triflate (**2.4Bb**) derivatives were found to be unaffected during the process of temperature variation, which showed that the silicon atom of chloro and triflate silyl pyridones were in true penta- and tetracoordinate states respectively. For example, the silicon-29 chemical shift of fluorodimethylsilylmethylpyrid-2-one (**2.7B**, Y=H) moved to about 8 ppm upfield when the NMR was recorded at  $-60^{\circ}\text{C}$  and to about 3 ppm low field at  $+54^{\circ}\text{C}$  (Table 2.7B). The silicon atom becomes more pentavalent at low temperature. On the other hand, the O-Si bond strength decreases at high temperature and hence the silicon atom converts to more tetravalent state as shown in Scheme 2.6B.



Scheme 2.6B

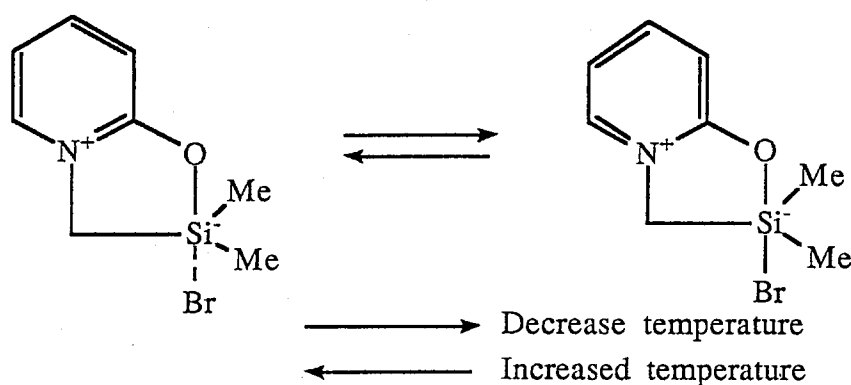
A similar explanations can be given for the bromo silyl pyridone (**2.5B**, Y=H). But instead of O-Si bond, the Si-Br bond strength increases at low temperature and decreases at high temperature as shown in Scheme 2.7B. The NMR values were shown in Table 2.8B.

**Table 2.8B**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR chemical shifts ( $\delta/\text{ppm}$ ) of bromodimethylsilylmethylpyrid-2-one (**2.5B**, Y=H) and bromodimethylsilylmethyl-6-methylpyrid-2-one (**2.5B**, Y=6-Me) at various temperatures.

Compound	Temp. ( $^{\circ}\text{C}$ )	NMR Data	
(2.5B, Y=H)	RT	$^1\text{H}$	0.72 (s, 6H, SiMe <sub>2</sub> ), 3.9 (s, 2H, NCH <sub>2</sub> ), 6.9-8.1 (m, 4H, arom)
		$^{13}\text{C}$	1.9, 44.8, 115.0, 115.7, 141.0, 146.1, 163.1
		$^{29}\text{Si}$	-18.4
	+54	$^1\text{H}$	0.70 (s, 6H, SiMe <sub>2</sub> ), 3.9 (s, 2H, NCH <sub>2</sub> ), 6.8-8.1 (m, 4H, arom)
		$^{13}\text{C}$	1.5, 44.7, 115.0, 115.7, 141.0, 146.1, 163.5
		$^{29}\text{Si}$	-10.0
	-50	$^1\text{H}$	0.70 (s, 6H, SiMe <sub>2</sub> ), 3.5 (s, 2H, NCH <sub>2</sub> ), 6.9-8.4 (m, 4H, arom)
		$^{13}\text{C}$	1.3, 44.0, 114.8, 116.0, 141.3, 146.9, 163.6
		$^{29}\text{Si}$	-24.6
(2.5B, Y=6-Me)	RT	$^1\text{H}$	0.45 (s, 6H, SiMe <sub>2</sub> ), 2.7 (s, 3H, Me), 3.7 (s, 2H, NCH <sub>2</sub> ), 6.8-8.0 (m, 3H, arom)
		$^{13}\text{C}$	1.7, 20.7, 37.9, 111.5, 115.2, 144.8, 151.6, 163.7
		$^{29}\text{Si}$	-21.3
	+60	$^1\text{H}$	0.43 (s, 6H, SiMe <sub>2</sub> ), 2.7 (s, 3H, Me), 3.6 (s, 2H, NCH <sub>2</sub> ), 6.9-8.3 (m, 3H, arom)
		$^{13}\text{C}$	1.6, 20.7, 37.6, 111.5, 115.2, 144.6, 151.4, 163.7
		$^{29}\text{Si}$	-14.2
	-50	$^1\text{H}$	0.41 (s, 6H, SiMe <sub>2</sub> ), 2.6 (s, 3H, Me), 3.5 (s, 2H, NCH <sub>2</sub> ), 7.0-8.5 (m, 3H, arom)
		$^{13}\text{C}$	1.0, 21.0, 36.8, 111.0, 115.2, 144.6, 150.7, 163.1
		$^{29}\text{Si}$	-31.6

**Table 2.9B**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  chemical shifts ( $\delta$ / ppm) of fluorodimethylsilyl-methyl-6-methylpyrid-2-one (**2.7B**, Y=6-Me) at various temperatures.

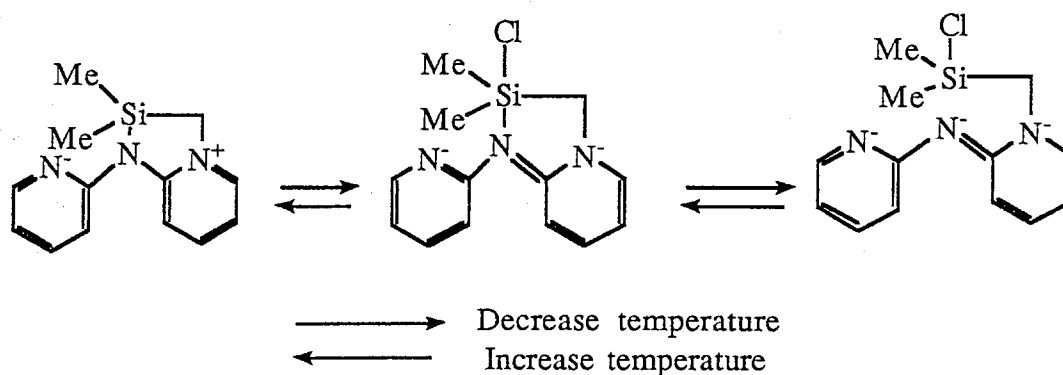
Compound	Temp. (°C)	NMR Data	
(2.7B, Y=6-Me)	RT	$^1\text{H}$	0.28 (d, $^3J_{\text{HSiF}}=5.9$ Hz, 6H, SiMe <sub>2</sub> ), 2.5 (s, 3H, Me), 3.0 (s, 2H, NCH <sub>2</sub> ), 6.5-7.5 (m, 3H, arom)
		$^{13}\text{C}$	2.4 (d, $^2J_{\text{CSiF}}=27.2$ Hz, SiMe), 20.9, 35.8 (d, $^2J_{\text{CSiF}}=50.5$ Hz, SiCH <sub>2</sub> ), 110.2, 112.5, 141.2, 148.6, 163.8
		$^{29}\text{Si}$	-35.5 (d, $^1J_{\text{SiF}}=252.9$ Hz)
	+54	$^1\text{H}$	0.27 (d, $^3J_{\text{HSiF}}=5.8$ Hz, 6H, SiMe <sub>2</sub> ), 2.4 (s, 3H, Me), 3.0 (s, 2H, NCH <sub>2</sub> ), 6.6-7.5 (m, 3H, arom)
		$^{13}\text{C}$	2.4 (d, $^2J_{\text{CSiF}}=27.0$ Hz, SiMe), 20.8, 35.8 (d, $^2J_{\text{CSiF}}=50.4$ Hz, SiCH <sub>2</sub> ), 110.0, 112.5, 141.1, 148.6, 163.8
		$^{29}\text{Si}$	-27.9 (d, $^1J_{\text{SiF}}=251.0$ Hz)
	-60	$^1\text{H}$	0.25 (d, $^3J_{\text{HSiF}}=5.7$ Hz, 6H, SiMe <sub>2</sub> ), 2.5 (s, 3H, Me), 3.1 (s, 2H, NCH <sub>2</sub> ), 6.8-7.9 (m, 3H, arom)
		$^{13}\text{C}$	2.6 (d, $^2J_{\text{CSiF}}=27.2$ Hz, SiMe), 21.1, 35.2 (d, $^2J_{\text{CSiF}}=51.8$ Hz, SiCH <sub>2</sub> ), 110.8, 111.9, 141.7, 148.6, 163.4
		$^{29}\text{Si}$	-39.3 (d, $^1J_{\text{SiF}}=250.0$ Hz)



Scheme 2.7B

We observed similar results with 6-Me derivative and the NMR values are shown in Tables 2.8B and 2.9B.

Our variable temperature results differ from the results observed by Kummer *et al*<sup>126</sup> in their dipyridyl derivatives. They have shown that the silicon atom becomes more four coordinate at low temperature and five coordinate at high temperature as shown in Scheme 2.8B. Their results were complete opposite to the results observed by us.



Scheme 2.8B

Reaction of silyl pyridones with nucleophiles have shown that chloro and bromo pyridones undergoes substitution while the fluoro derivative was inert towards nucleophiles. When 0.5 equivalent of NMI was added to chlorodimethylsilylmethylpyridone (**2.4Ba**, Y=H) the signal that appeared at -41.1 ppm in silicon-29 NMR disappeared completely, instead a slightly broad peak at -48.8 ppm was observed, which indicated the formation of the substitution product. Although NMI reacts readily with  $\text{Me}_3\text{SiCl}$ , but the equilibrium lies far to the side of Si-Cl. There was a rapid equilibrium between the complex in solution and the starting chlorosilane as a consequence of nucleophilic attack of the chloride counterion at the silicon atom of the substituted product, thereby regenerating the silyl chloride and free NMI. That 1 equivalent of NMI gave substitution product almost exclusively and this was confirmed by a sharp signal in silicon-29 NMR at -54.2 ppm (Table 2.4A). The possible explanations for the high reactivity of the silyl chloride (**2.4Ba**, Y=H) could be a longer Si-Cl bond in a 'semi ionic' state due to high polarisability of the chloride atom, as observed recently in some pentacoordinated complexes<sup>20,60,127</sup>, or it may be due to a weakly bound ligand Cl opposite to a strongly bound ligand O, where the more strongly bound ligand oxygen pushes the more weakly bound ligand chlorine away and make the Si-Cl bond longer than the normal Si-Cl bond<sup>128</sup>. In addition, it has been shown that the Si-Cl bond can be stretched by approximately 17%<sup>129</sup>. Similar result was obtained when bromo silyl pyridone (**2.5B**, Y=H) was treated with NMI (Table 2.10B) and a similar explanations can be put forward for its reactivity.

Fluoro silyl pyridone was found to be inert towards NMI or HMPA. No reaction was taking place when fluorodimethylsilylmethylpyrid-2-one (**2.7B**, Y=H) was treated with NMI or HMPA (Tables 2.11B and 2.12B). The probable explanation could be that the two ligands from the same period (here oxygen and fluorine)

shares the electron density in such a way that both ligands are fairly tightly bound to silicon, which makes the Si-F stronger and hence inert to substitution<sup>128</sup>.





Table 2.11B Interaction between fluorodimethylsilylmethylpyrid-2-one (2.7B, Y=H) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (2.7B, Y=H) : NMI			
		1:0	1:0.5	1:1	0:1
$^1\text{H}$	H-2	--	7.4	7.4	7.4
	H-4	--	7.0	7.0	7.0
	H-5	--	6.9	6.8	6.9
	NCH <sub>3</sub>	--	3.7	3.7	3.7
	H-3	6.4	6.4	6.4	--
	H-4	7.6	7.6	7.6	--
	H-5	6.6	6.6	6.6	--
	H-6	7.4	7.4	7.4	--
	NCH <sub>2</sub>	3.2	3.2	3.1	--
	SiCH <sub>3</sub>	0.32 d	0.32 d	0.31 d	--
	$^3\text{J}_{\text{HF}}$	6.8 Hz	6.8 Hz	6.8 Hz	--
$^{13}\text{C}$	C-2	--	137.8	137.8	137.8
	C-4	--	129.3	129.4	129.5
	C-5	--	120.2	120.1	120.1
	NCH <sub>3</sub>	--	33.2	33.2	33.3
	C-2	163.2	163.1	163.0	--
	C-3	109.2	109.2	109.1	--
	C-4	139.1	139.0	139.0	--
	C-5	116.8	116.8	116.8	--
	C-6	141.4	141.4	141.4	--
	NCH <sub>2</sub>	39.5 d	39.5 d	39.5 d	--
	$^2\text{J}_{\text{CF}}$	44.0 Hz	44.0 Hz	44.1 Hz	--
	SiCH <sub>3</sub>	1.8 d	1.8 d	1.8 d	--
	$^2\text{J}_{\text{CF}}$	24.6 Hz	24.5 Hz	24.5 Hz	--
$^{29}\text{Si}$	SiCH <sub>3</sub>	-22.3 d	-22.2 d	-22.3 d	--
	$^1\text{J}_{\text{SiF}}$	256.8 Hz	256.6 Hz	256.7 Hz	--
Quantities used:					
Pyridone (mmol)		2	2	2	--
NMI (mmol)		--	1	2	2
Solvent : CDCl <sub>3</sub> , 2.0 ml					

Table 2.12B Interaction between fluorodimethylsilylmethylpyrid-2-one (2.7B, Y=H) and hexamethylphosphoramide (HMPA) : NMR Data

$\delta$ (ppm)		Ratio of (2.7B, Y=H) : HMPA			
		1:0	1:0.5	1:1	0:1
$^1\text{H}$	NCH <sub>3</sub>	--	2.8 d	2.8 d	2.8 d
	$^3\text{J}_{\text{PH}}$	--	9.3 Hz	9.2 Hz	9.3 Hz
	H-3	6.4	6.4	6.4	--
	H-4	7.6	7.5	7.6	--
	H-5	6.6	6.6	6.6	--
	H-6	7.4	7.3	7.4	--
	NCH <sub>2</sub>	3.2	3.1	3.1	--
	SiCH <sub>3</sub>	0.32 d	0.31 d	0.32 d	--
	$^3\text{J}_{\text{HF}}$	6.8 Hz	6.8 Hz	6.8 Hz	--
$^{13}\text{C}$	NCH <sub>3</sub>	--	36.7 d	36.6 d	36.7 d
	$^2\text{J}_{\text{PC}}$	--	3.9 Hz	3.8 Hz	3.9 Hz
	C-2	163.2	163.2	163.1	--
	C-3	109.2	109.2	109.2	--
	C-4	139.1	139.0	139.1	--
	C-5	116.8	116.7	116.6	--
	C-6	141.4	141.4	141.2	--
	NCH <sub>2</sub>	39.5 d	39.5 d	39.5 d	--
	$^2\text{J}_{\text{CF}}$	44.0 Hz	44.0 Hz	44.1 Hz	--
	SiCH <sub>3</sub>	1.8 d	1.8 d	1.7 d	--
$^{29}\text{Si}$	$^2\text{J}_{\text{CF}}$	24.6 Hz	24.6 Hz	24.6 Hz	--
	SiCH <sub>3</sub>	-22.3 d	-22.8 d	-22.9 d	--
	$^1\text{J}_{\text{SiF}}$	256.8 Hz	256.9 Hz	257.0 Hz	--
Quantities used :					
Pyridone (mmol)		2	2	2	--
HMPA (mmol)		--	1	2	2
Solvent : CDCl <sub>3</sub> , 2.0 ml					

## ***CHAPTER THREE***

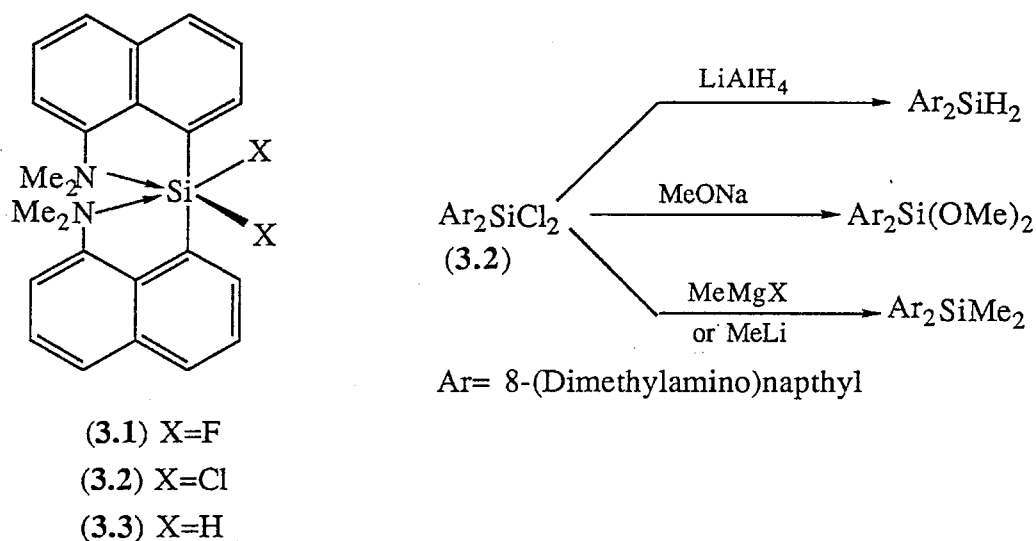
### ***Coordination and Reactivity at Silicon***

### 3.1 INTRODUCTION:

It has been known for a long time that silicon can expand its valence shell. Several types of penta and hexacoordinated silicon compounds have been reported, in which the silicon is surrounded by electronegative ligands<sup>30,38,95,96,130</sup> and more recently by nonelectronegative ligands<sup>86</sup>. Numerous structural studies of hypervalent silicon complexes have been reported<sup>30,38,49,86,95,130-132</sup>.

As described in the introduction recently much interest has been paid to the existence<sup>55,85</sup>, reactivity<sup>51,87-94</sup> and isomerisations<sup>55,95</sup> of pentavalent silicon derivatives that have been proposed as intermediates in reactions of organosilanes in solution<sup>95</sup>. It is reported<sup>119,133</sup> that the reactivity of pentacoordinate silicon species is quite different from those of their tetracoordinated analogues. Corriu and co-workers<sup>89</sup> reported that  $K^+$ , 18-Crown-6 salts of  $[PhMeSiF_3]^-$  and  $[Ph_3SiF_2]^-$  are much more reactive than  $PhMeSiF_2$  and  $Ph_3SiF$  with Grignard reagents  $RMgX$ , to give  $PhMe(F)SiR$  and  $Ph_3Si(R)$  respectively. Similar enhanced reactivity was observed for reaction of these two anionic silicates with other nucleophiles,  $LiAlH_4$ ,  $RLi$ ,  $RO^-$ ,  $NaBH_4$ . They have suggested<sup>89</sup> that the enhanced reactivity might arise from a greater electropositive character of the pentacoordinated silicon atom. Again, the reactivity of hexacoordinated silicon compounds was quite different from that of tetra and pentavalent silicon compounds i.e., the basic transformations of Si-F, Si-Cl and Si-H in hexacoordinated silicon species are completely different from those observed with the corresponding tetra and pentacoordinated compounds. Corriu *et al*<sup>103</sup> have found that the reactivities of bis(8(dimethylamino)naphthyl) of silicon complexes **3.1** and **3.2** with nucleophiles were different. Difluorosilane **3.1** appears to be completely inert to any nucleophilic

reagents ( $\text{LiAlH}_4$ ,  $\text{RMgX}$ ,  $\text{RLi}$ ) whereas dichlorosilane **3.2** is substituted very easily by nucleophiles (Scheme 3.1).



Scheme 3.1

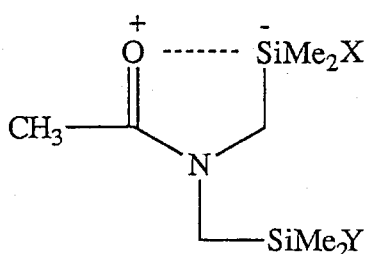
The lack of reactivity of fluorosilane (**3.1**) could be attributed to both the minimal elongation of the Si-F bonds and a maximal hindrance around the silicon atom. The reactivity of hydrosilane (**3.3**) towards nucleophiles is again very different from that observed for **3.1** and **3.2**. It is chemically inert towards strong nucleophiles ( $\text{RLi}$ ,  $\text{RMgX}$ ), whereas organolithium reagents are able to substitute the Si-H bond in tetra- and pentacoordinate silicon compounds<sup>104-106</sup>. Furthermore, those reagents that have been reported to react efficiently with the pentacoordinate dihydrosilanes such as sulphur, carbon disulphide<sup>134</sup>, carbonyl groups<sup>119</sup> or acid derivatives<sup>133</sup> exhibit no reactivity towards compound **3.3**.

The reactivity of hexacoordinated silicon compounds are found to be quite different from that of either penta- or tetracoordinated silicon compounds. Our interest in the reactivity of pentacoordinated silicon species is derived from several sources:-

- (i) Nucleophilic displacements in tetravalent organosilicon derivatives,  $R_3SiX$ , have been assumed to pass through the formation of a pentacoordinated anionic silicon intermediate<sup>7</sup>.
- (ii) The silicon atom can be activated during nucleophilic substitution by a catalytic amount of nucleophiles which are good coordinating agents for silicon<sup>7</sup>.
- (iii) As we mentioned in chapter two, we observed very interesting results when NMI was added to mono, di and trichlorosilylpyridones. Monochlorosilylpyridone gave only substitution product, while dichlorosilylpyridone gave mixtures of substitution and addition products. Addition of NMI to trichlorosilylpyridone gave exclusively addition product (Chapter 2).
- (iv) Chloro and bromosilylpyridones were found to be reactive towards nucleophiles, NMI, HMPA while silylfluoride was inert to nucleophiles (Chapter 2).
- (v) The reaction of silicon hydrides,  $RSiH_3$  and  $R_2SiH_2$  with  $KH$  as a catalyst gives redistribution processes that are interpreted as involving intermediate formation of a pentacoordinated silicon complexes<sup>135</sup>.
- (vi) The reduction of carbonyl compounds with silicon hydrides and fluoride<sup>136-139</sup> or alcoholate<sup>140,141</sup> ions as activators is well known and proceeds through a pentacoordinate silicon intermediate.
- (vii) The transfer of an allyl group to a carbonyl compound from an allyl silane activated by fluoride ion ( $n-Bu_4N^+F^-$ )<sup>142-144</sup>. Furthermore, isolated pentacoordinated allyl derivatives may undergo allyl group transfer to a carbonyl compound<sup>94</sup>.
- (viii) It has been found that organobis(benzene-1,2-diolato)complexes of silicon<sup>103</sup>  $RSi(o-O_2C_6H_4)_2 Na^+$  and hydridoalkoxosiliconates  $H_nSi(OR)_{5-n}^- K^+$ , ( $n=1, 2$ )<sup>106,145</sup> derivatives are very reactive towards nucleophilic reagents e.g., organometallic compounds,  $RMgX$ <sup>106,142-145</sup>,  $RLi$ <sup>142-144</sup> and hydrides<sup>142-144</sup>.

In continuation of our work on the reactivity of silyl pyridones towards different nucleophiles we were interested to explore further the possible transformations in the case of neutral pentacoordinated species, particularly towards different nucleophilic reagents.

Most of the work on the reactivity of tetra- and hypervalent silicon compounds with different nucleophiles has been studied by Corriu and co-workers and has shown that each system behaves quite differently towards a particular nucleophile. But they have studied the reactivity of each system separately. We were interested to find a system where both four and five coordinated silicon atoms are present in the same molecule and to compare their reactivity towards different nucleophiles. We used the compound **3.4**, which is an acetamide derivative, for our study. Although the compound was first prepared by Lasocki<sup>146</sup>, its structure was initially incorrectly assigned but this was modified and the correct structure was proved by Yoder<sup>58</sup> in 1978. The chemistry of this type of compound was almost completely unknown before the work presented here.



(3.4)

The molecule contains both four and five coordinate silicon atoms which will provide a probe for reactivity of the two types of silicon atoms under identical

conditions. We expected that the two silicon atoms are sufficiently isolated from one another to behave independently and their existence is long enough on the NMR time scale to compare their reactivity. The main aim of this work was to study-

(A) The relative ability of leaving groups to stabilize pentacoordinate silicon atom (when  $X \neq Y$ ) and

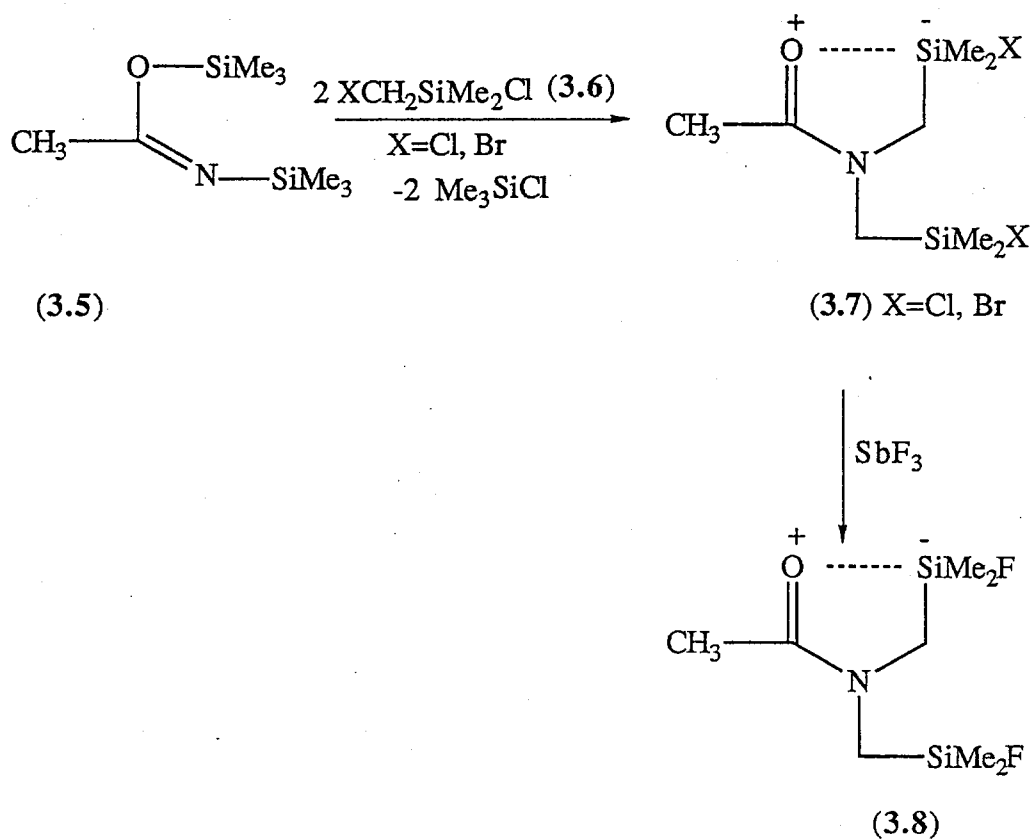
(B) The relative reactivity to nucleophilic substitution of four and five coordinate silicon (when  $X = Y$ ).

The reactivity to nucleophilic substitution of four and five coordinate silicon has been studied by silicon-29 NMR. The method involved the addition of a nucleophile such as NMI or HMPA to the bis-silicon amide and to record the changes in the NMR spectra with varying amounts of nucleophile. It will be shown that five coordinate silyl chloride and bromide were found to be more reactive than the four coordinate silyl chloride and bromide. But four coordinate silyl fluoride was more reactive than the five coordinate silyl fluoride.

### **3.2 RESULTS AND DISCUSSION:**

When 1 equivalent of bis(trimethylsilyl)acetamide (3.5) was treated with 2 equivalents of halomethyldimethylchlorosilane (3.6), bis(halodimethylsilylmethyl)acetamides (3.7) were obtained with liberation of 2 equivalents of chlorotrimethylsilane. The fluoro derivative (3.8) was prepared by treating either chloro or bromo silyl acetamide (3.7) with antimony trifluoride as shown in Scheme 3.2

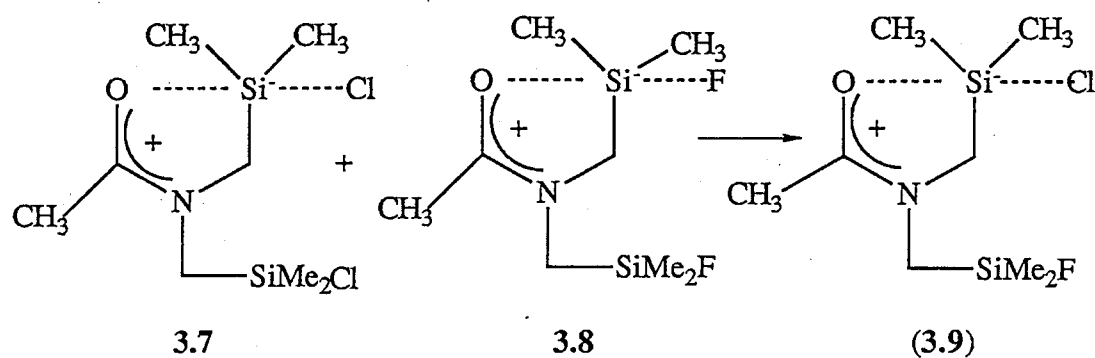




Scheme 3.2

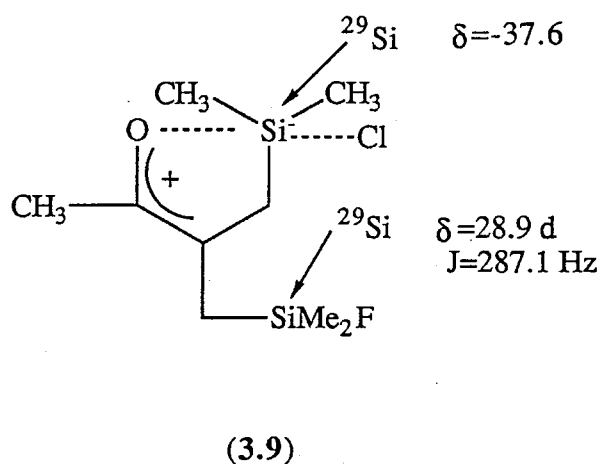
### A) ABILITY OF LEAVING GROUPS TO STABILIZE PENTACOORDINATE SILICON

When equal moles of silyl fluoride (3.8) and silyl chloride (3.7, X=Cl) were mixed in  $\text{CDCl}_3$  exchange of halogens were taking place between four coordinate Si-Cl and five coordinate Si-F and a new compound of the type (3.9) was obtained (Scheme 3.3). Similarly (3.10) (Scheme 3.4) and (3.11) (Scheme 3.5) were obtained.



Scheme 3.3

There were two signals in the silicon-29 NMR spectrum of silyl chloride (3.7, X=Cl) one signal at -39.9 ppm was assigned for pentacoordinate silicon and the other at 26.8 ppm was due to tetracoordinate silicon. We observed two doublets for silyl fluoride (3.8) in the silicon-29 NMR. One doublet at -23.5 ppm with Si-F coupling constant 256.8 Hz was for the pentacoordinate silicon and the other doublet at 28.9 ppm with Si-F coupling constant 287.1 Hz for the tetracoordinate silicon atom. When equimolar amounts of silyl chloride and silyl fluoride were mixed, we observed only 2 signals in the silicon-29 NMR. One singlet at -37.6 ppm and a doublet at 28.9 ppm with Si-F coupling constant 287.1 Hz suggested the compound (3.9) (Scheme 3.3)

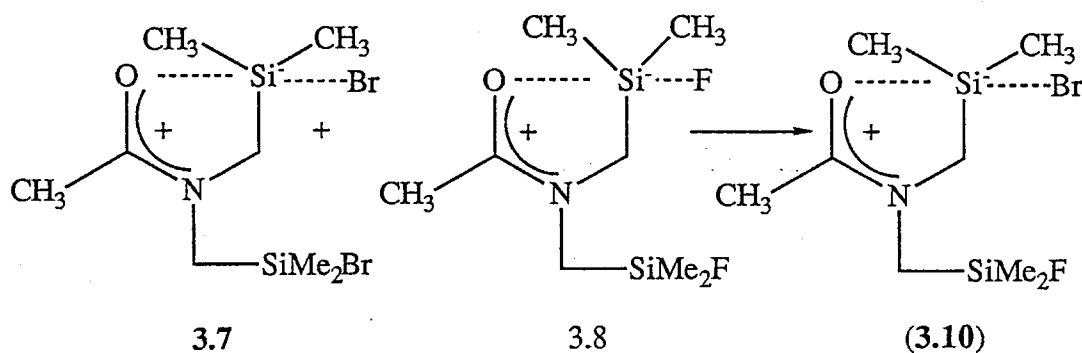


These signals are definitely due to **3.9** which was isolated as solid. They cannot be from rapid equilibrium between silyl fluoride (**3.8**) and silyl chloride (**3.7**, X=Cl) because-

- (i) Si-F coupling was maintained for the four coordinate species,
- (ii) There were only two signals and
- (iii) The -37.6 ppm signal cannot be an average of -39.9 and -23.5 ppm.

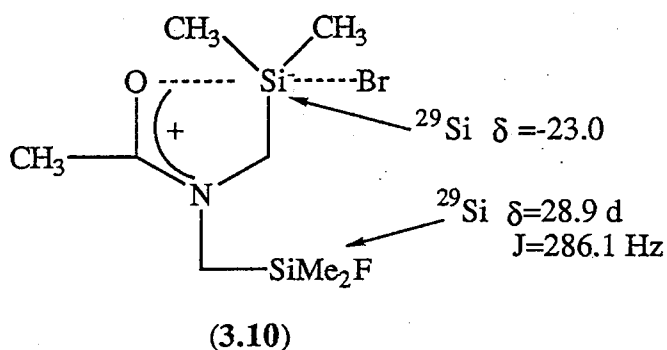
The silicon-29 NMR showed that the exchange of halogens were taking place between the four coordinate Si-Cl and five coordinate Si-F. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR values of **3.9** are shown in Table 3.1 at the end of the chapter. The above experiment indicated that chlorine has greater ability to stabilize a pentacoordinate silicon atom than fluorine.

Similarly, when equal moles of silyl bromide (**3.7**, X=Br) were mixed with silyl fluoride (**3.8**) we obtained the new compound (**3.10**) (Scheme 3.4). Exchange of



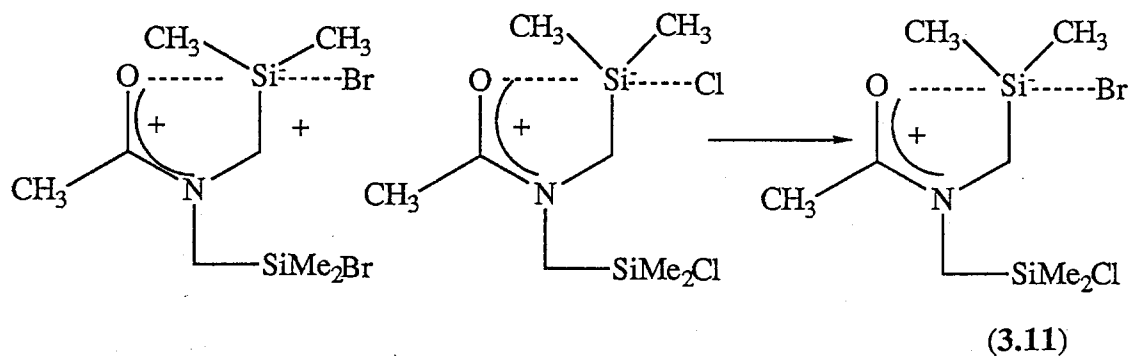
Scheme 3.4

halogens took place between four coordinate Si-Br and five coordinate Si-F. The singlet at -23.0 ppm was due to pentacoordinate silicon and the doublet



at 28.9 ppm with Si-F coupling constant 286.1 Hz was for tetracoordinate silicon. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR values of (3.10) are shown in Table 3.2. Like chlorine, bromine too has greater ability to stabilize pentacoordinate silicon than fluorine.

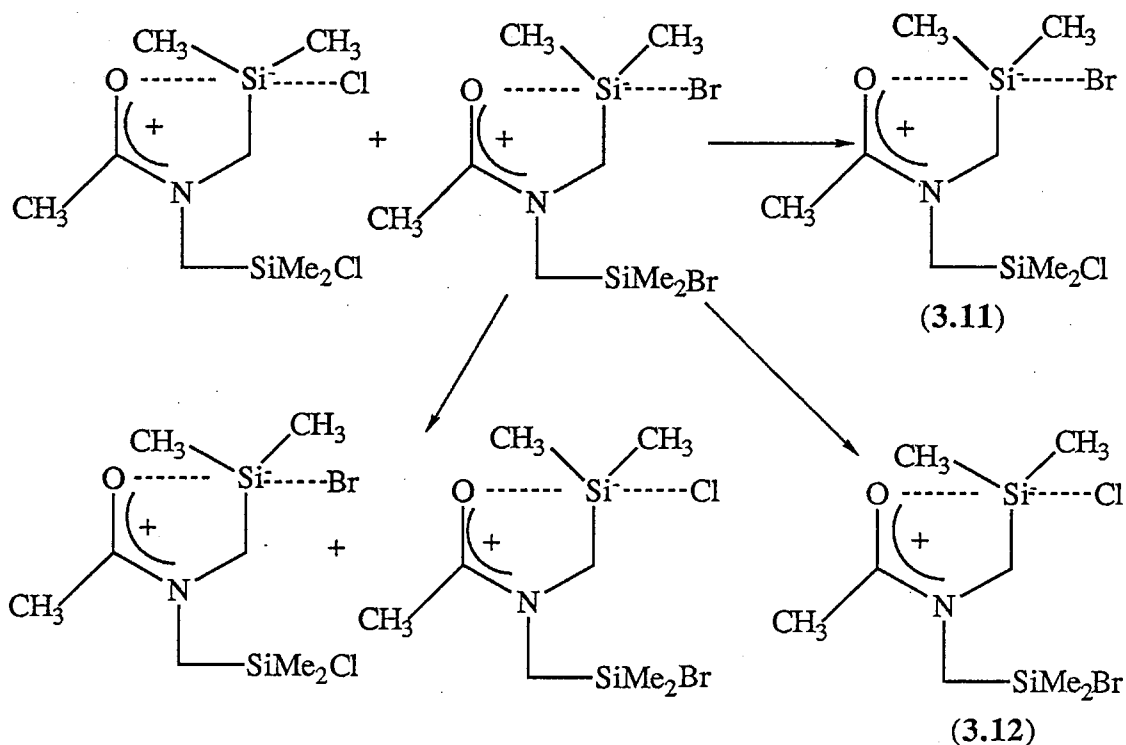
Exchange of halogens between silyl fluoride with chloride (Scheme 3.3) and bromide (Scheme 3.4) were quite straightforward, but the exchange of halogens between silyl chloride (3.7, X=Cl) and bromide (3.7, X=Br) were more difficult to interpret.



Scheme 3.5

Addition of equal moles of each can give rise to three possibilities as shown in Scheme 3.6. Addition of equal moles of silyl chloride and bromide gave two signals

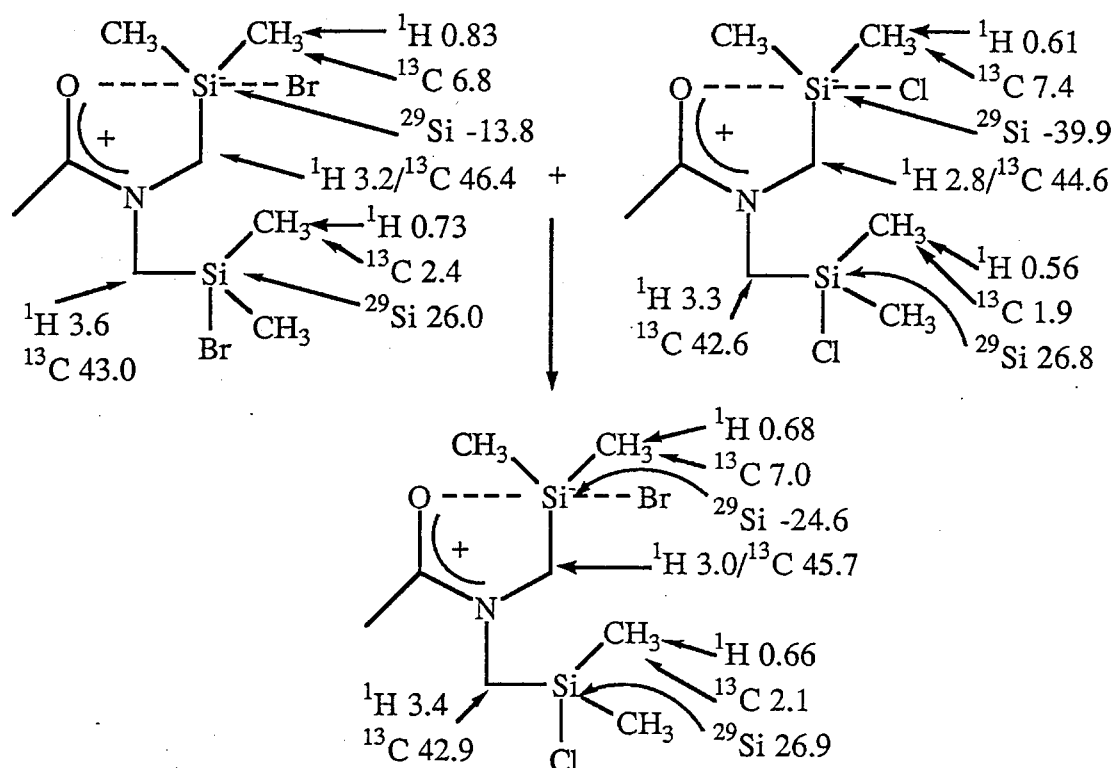
in silicon-29 NMR. A peak at -24.6 ppm was for pentacoordinate silicon and the other at 26.9 ppm due to tetracoordinate silicon. If exchange of halogens had taken



**Scheme 3.6** Possibilities of exchange of halogens between silyl chloride and silyl bromide.

place between pentacoordinates Si-Br and Si-Cl (Scheme 3.6) then we would have got a mixture of two different compounds and observed two signals in pentacoordinate silicon region, one for pentacoordinate Si-Br and the other for pentacoordinate Si-Cl. But we observed only one signal in the pentacoordinate silicon region. Therefore, we ruled out the possibility of slow exchange of halogens between two pentavalent silicon atoms. The two other possibilities are that exchange of halogens can take place between four and five coordinate silicons and can give rise to (3.11) or (3.12) as shown in Scheme 3.6. It was difficult to

differentiate between (3.11) and (3.12) by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR, although the chemical shifts are more consistent with 3.11 than 3.12 (e.g.,  $^{29}\text{Si}$  of 3.12 should be about -40 ppm), but it could be an average between the two species.



## **B) REACTIONS OF BIS(HALODIMETHYLSILYLMETHYL)ACETAMIDE WITH NUCLEOPHILES (e.g. NMI and HMPA)**

### Reaction of bis(halodimethylsilylmethyl)acetamide with NMI

Reactivity of bis(halodimethylsilylmethyl)acetamide with NMI were examined by adding successive aliquots of NMI to a solution of silicon compounds, under nitrogen, in an NMR tube and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were recorded after

each addition. N-methylimidazole is a powerful nucleophile and forms stable four coordinate ionic adducts with silanes<sup>78</sup>. Although NMI reacts readily with Si-halogen, the equilibrium lies far to the side of Si-Cl for most  $R_3SiCl$  such as  $Me_3SiCl$ ,  $Et_3SiCl$ ,  $Ph_3SiCl$ .

The information concerning the structural changes were based on the  $^{29}Si$  chemical shifts and on the proton NMR of NMI compared to the uncomplexed NMI. The protons at positions C-2, C-4 and C-5 signals were shifted to downfield due to complexation of NMI with silicon. The effect was highest for the proton attached to C-2. Addition of excess NMI induced upfield shift of NMI resonances which is due to chemical exchange between the free and complexed NMI. The lone pair of electrons on nitrogen atom of NMI forms the dative Si-N bond and the imidazolium cation becomes deshielded which is most pronounced at the C-2 position as shown in Figure 3.1 by the following resonance structures.

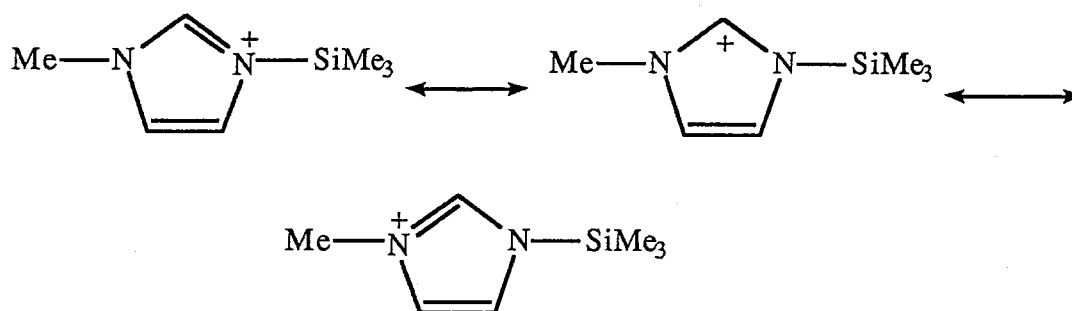


Figure 3.1 Resonance structure of NMI on complexation.

The changes in the chemical shifts of NMI in both proton and carbon-13 NMR spectra follow the analogous trend observed by Pugmire<sup>147</sup> as well as Batterham<sup>148</sup> for the protonation of imidazole by hydrogen chloride.

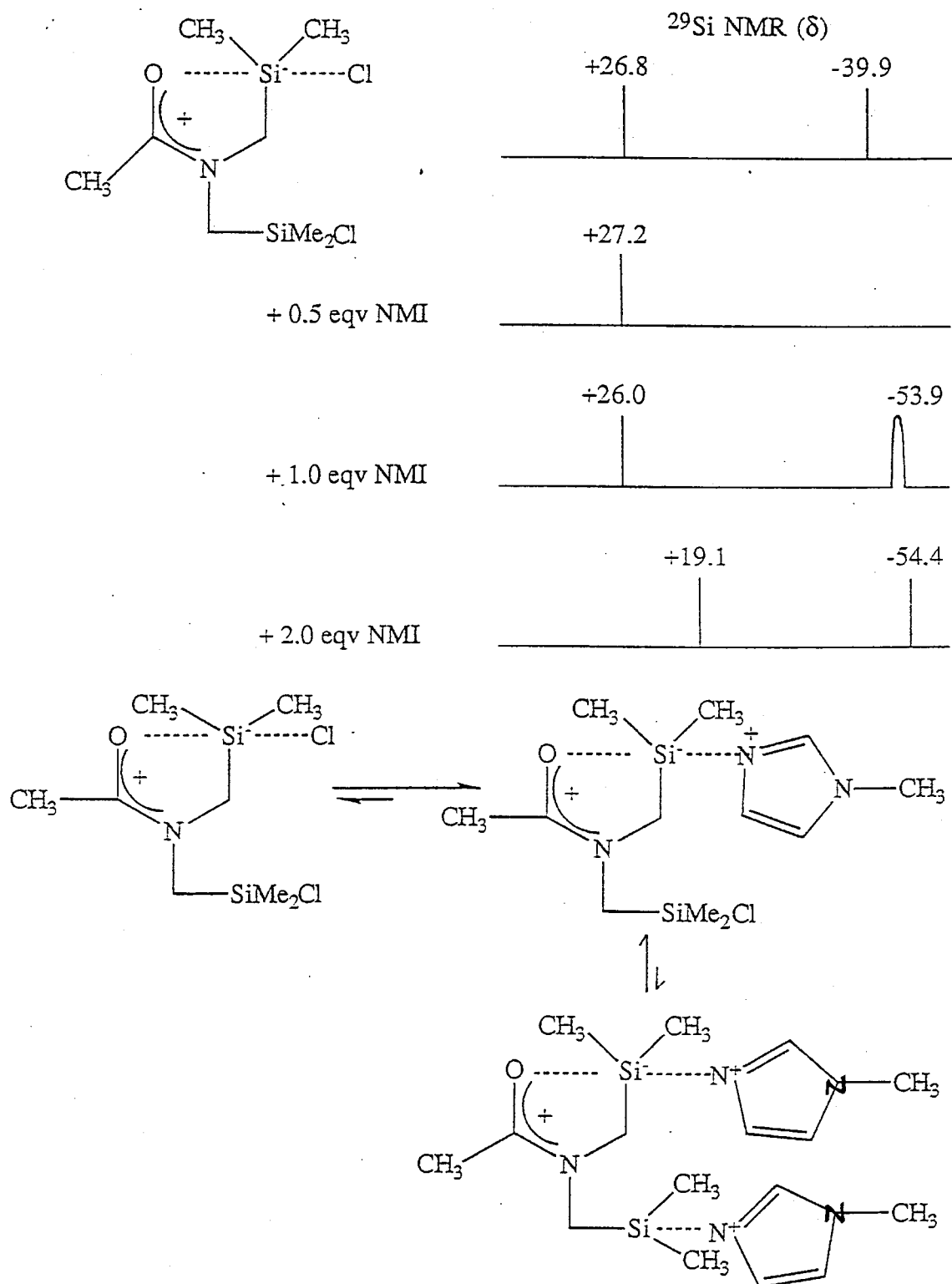
Reaction of bis(chlorodimethylsilylmethyl)acetamide (3.7, X=Cl) with NMI

The X-ray crystal structure of bis(chlorodimethylsilylmethyl)acetamide has been reported by Yoder<sup>58</sup> and it was found that one silicon atom is pentacoordinate and the other is tetracoordinate. The silicon-29 chemical shift of the pentacoordinate atom shows a signal at -39.9ppm and the tetracoordinate silicon atom appears at 26.8 ppm. When 0.5 equivalent of NMI was added to it, the signal that initially appeared at -39.9 ppm disappeared completely which indicated that substitution was taking place at the pentacoordinate silicon atom. This is consistent with an intermediate rate equilibrium between the complex in solution and the starting chlorosilane as a consequence of nucleophilic attack of the chloride counterion at the silicon atom of the substituted product, thereby regenerating the silyl chloride and free NMI as shown in Scheme 3.7. When 1 equivalent of NMI was added a slightly broad peak at -53.9 ppm was observed. The upfield shift of the silicon-29 peak showed that equilibrium lies more towards substitution. That excess of NMI gave the substitution product almost exclusively was confirmed by a sharp signal in silicon-29 NMR at -54.4 ppm (Scheme 3.7) (Table 3.3). No line broadening was observed for the NMI resonances, showing NMI to be exchanging rapidly with the complex. The equilibrium between silyl chloride and the substituted product was sufficiently rapid on the NMR time scale, so there was only one resonance for each of the carbon and proton atoms in any mixture between them. The <sup>29</sup>Si resonance for the four coordinate silicon at an NMI to complex ratio of 2:1 shows an upfield shift to 19.1 ppm indicating that it is now complexed with the NMI. But this reaction follows reaction at the five coordinate silicon.



Scheme 3.7 Interaction between bis(chlorodimethylsilylmethyl)acetamide (3.7.

X=Cl) and NMI



Reaction of bis(chlorodimethylsilylmethyl)acetamide (3.7, X=Cl) with HMPA

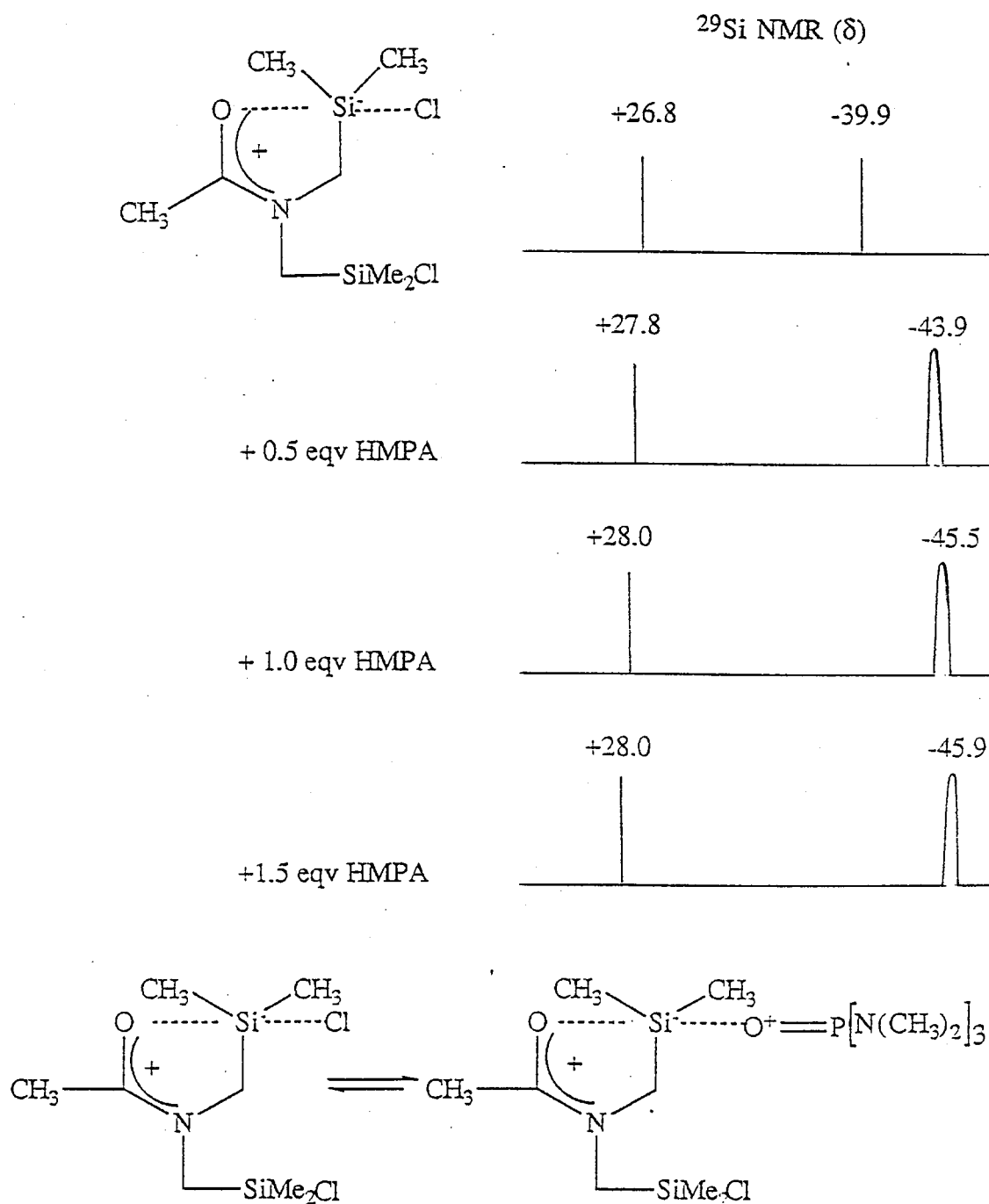
We observed a similar result as for NMI when HMPA was added to bis(chlorodimethylsilylmethyl)acetamide. Like NMI, HMPA attacked the pentacoordinate silicon atom and gave the substitution product (Table 3.4). A slight broad peak in silicon-29 NMR was observed when HMPA was added to silyl chloride. A gradual but small upfield shift of the silicon-29 NMR was recorded as the concentration of HMPA increased, indicating that the equilibrium lies towards the side of substitution. The absence of any coupling between the phosphorus atom of HMPA and silicon atom, together with a slightly broad peak showed that the life time of the HMPA complexes are usually shorter i.e., the rate of the back reaction is fast because presumably HMPA is a better leaving group from silicon. The four coordinate Si-Cl bond was unaffected even in presence of excess HMPA (Scheme 3.8).

Reaction of bis(bromodimethylsilylmethyl)acetamide (3.7, X=Br) with NMI

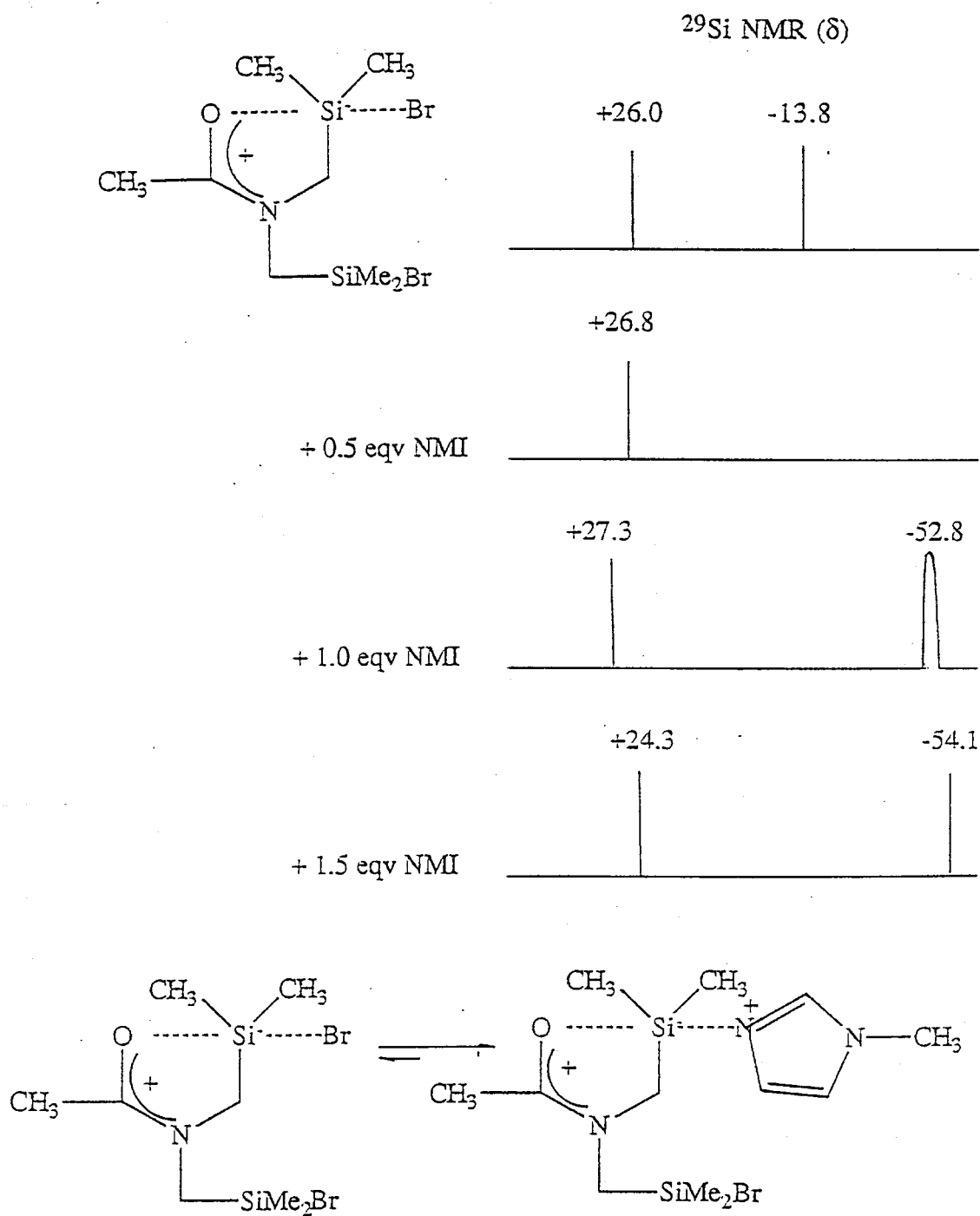
We found two signals for the bis(bromodimethylsilylmethyl)acetamide in the silicon-29 NMR. The peak at +26.0 ppm was for the tetracoordinate silicon and the peak at -13.8 ppm was for the pentacoordinate silicon. Compared to silyl chloride (3.7, X=Cl), the silyl bromide showed quite a low value for five coordinate silicon. It is probably because, either-

- (i) The Si-Br bond is stretched i.e., on its way to O-Si and Br<sup>-</sup>, or
- (ii) There is an equilibrium  $\text{O} \cdots \text{Si} - \text{Br} \rightleftharpoons \text{O} - \text{Si} + \text{Br}^-$ . These can not at present be distinguished.

Scheme 3.8 Interaction between bis(chlorodimethylsilylmethyl)acetamide (3.7, X=Cl) and HMPA



Scheme 3.9 Interaction between bis(bromodimethylsilylmethyl)acetamide (3.7, X=Br) and NMI

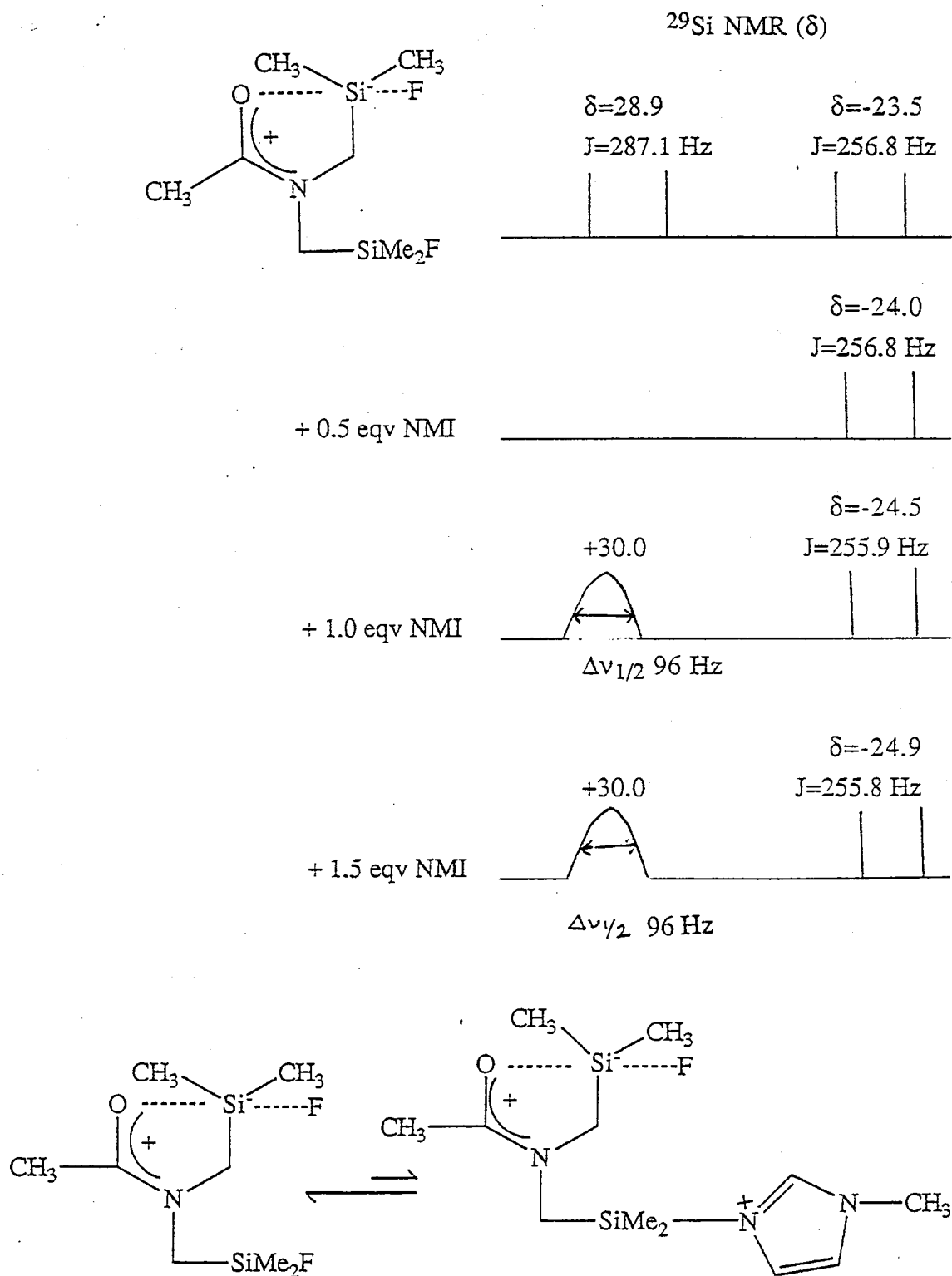


Bis(bromodimethylsilylmethyl)acetamide also gave a substitution product with NMI. Like the chloride analogue, the NMI attacked the five coordinate silicon atom without affecting the four coordinate Si-Cl bond even in presence of excess NMI (Scheme 3.9). The upfield shift of the silicon-29 peak from -13.8 ppm to -54.1 ppm for the substituted product, together with increased deshielding of the NMI in proton resonance, particularly at C-2 position, confirmed the formation of the dative Si-N bond (Table 3.5). The equilibrium between the silyl bromide and the substituted product was rapid on the NMR time scale, so there was only one set of resonances for each of the carbon and proton atoms in any mixture between them. The successive increases in the concentration of NMI drives the equilibrium in favour of the substitution (Scheme 3.9).

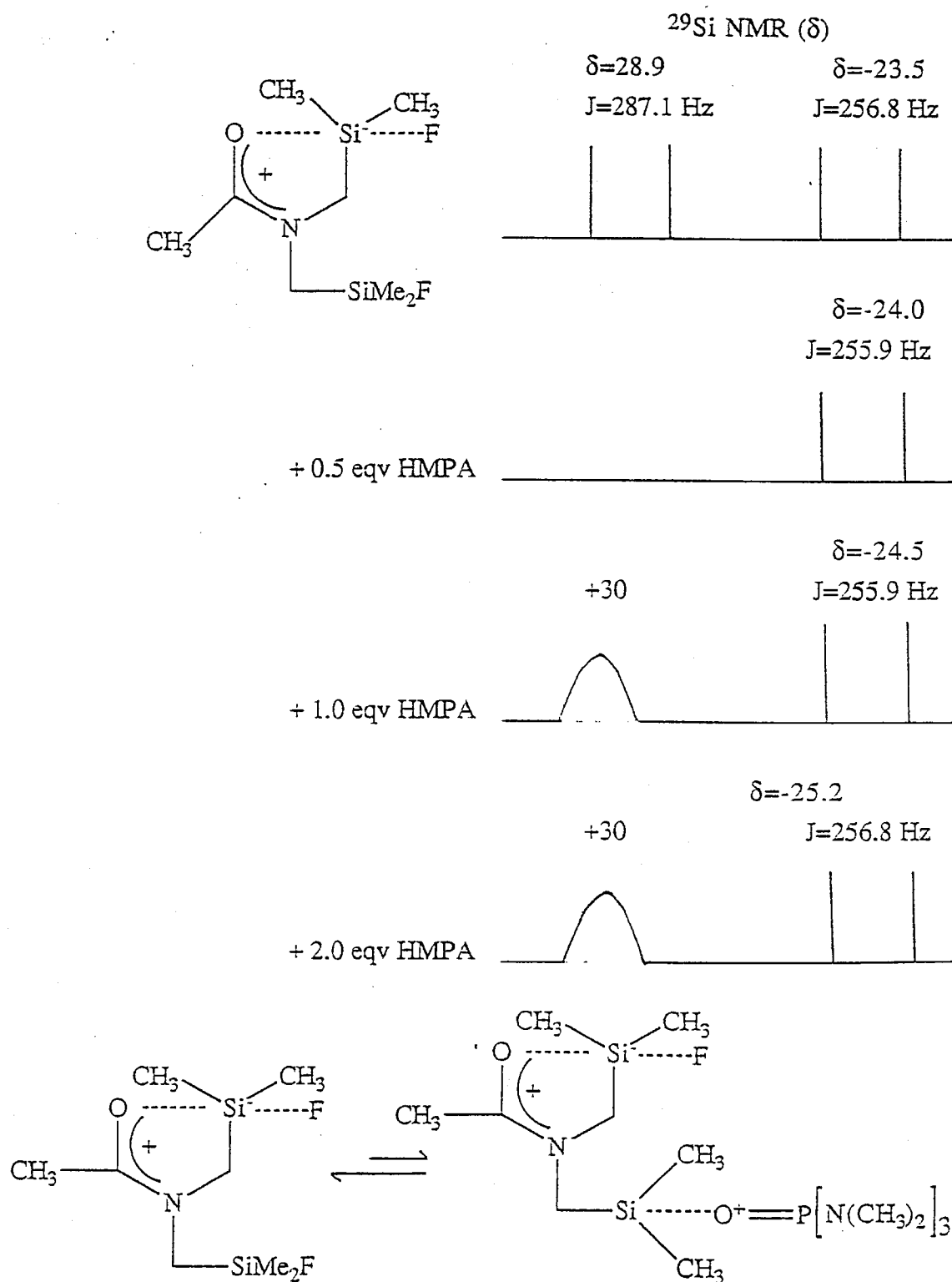
#### Reaction of bis(fluorodimethylsilylmethyl)acetamide (3.8) with NMI and HMPA

We found two doublets for the silyl fluoride (3.8) in the silicon-29 NMR. One doublet at -23.5 ppm with Si-F coupling constant 256.8 Hz was for the pentacoordinate silicon atom and the other at 28.9 ppm with Si-F coupling constant 287.1 Hz was due to tetracoordinate silicon atom. Its behaviour towards NMI and HMPA was unexpected and different from that of silyl chloride and bromide. When 0.5 equivalent of NMI was added to it, the doublet and Si-F coupling which appeared at 28.9 ppm in silicon-29 NMR before the addition of NMI disappeared completely. This proved that a reaction was taking place at tetracoordinate silicon. When an excess NMI was added, no shifting of silicon-29 NMR either to high or low field was observed (Table 3.6). Instead a broad peak at 30 ppm without Si-F coupling was found, indicating that the equilibrium was towards the starting material as shown in Scheme 3.10. Deshielding of NMI in proton resonance, particularly at C-2 position was not observed. This confirmed the absence of a

**Scheme 3.10** Interaction between bis(fluorodimethylsilylmethyl)acetamide (3.8) and NMI



Scheme 3.11 Interaction between bis(fluorodimethylsilylmethyl)acetamide (3.8) and HMPA



significant quantity of substitution product. The five coordinate silicon atom was found to be unaffected even in the presence of excess NMI.

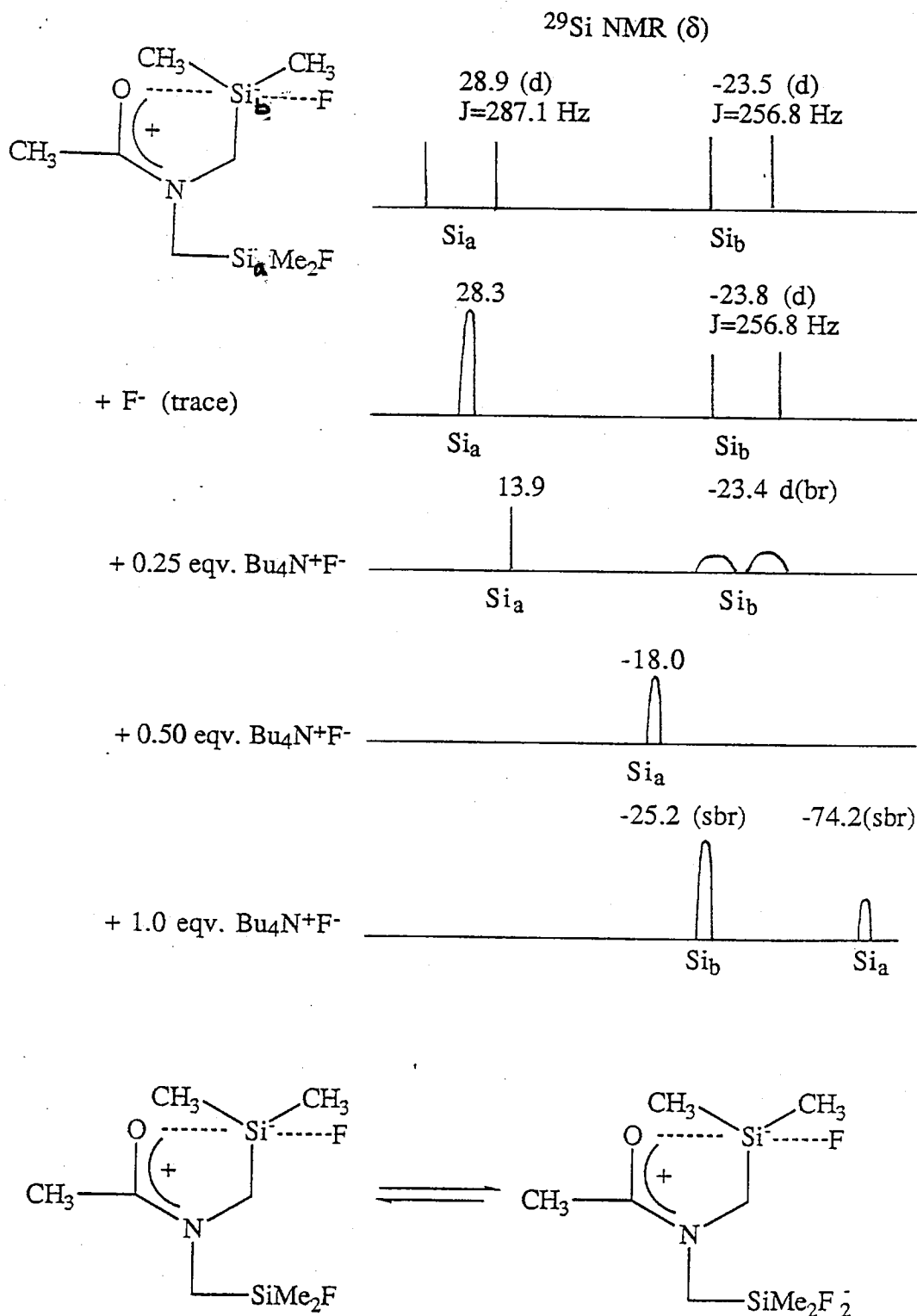
An exactly similar result was obtained when silyl fluoride (3.8) was treated with HMPA (Scheme 3.11). The absence of any coupling between the phosphorus atom of HMPA and silicon atom, together with unchanged chemical shifts in the silicon-29 NMR spectrum with a broad peak are entirely consistent with the absence of any significant amounts of substitution product (Table 3.7)

Reaction of bis(fluorodimethylsilylmethyl)acetamide (3.8) with tetrabutyl ammonium fluoride ( $\text{Bu}_4\text{N}^+\text{F}^-$ )

When a catalytic amount of  $\text{Bu}_4\text{N}^+\text{F}^-$  was added to silyl fluoride (3.8) the doublet at 28.9 ppm with Si-F coupling disappeared completely, instead a broad peak at 28.3 ppm was observed. The doublet at -23.5 ppm was unaffected and the Si-F coupling constant 256.8 Hz was maintained, which clearly showed that the  $\text{F}^-$  ion has attacked the tetracoordinate silicon atom and the equilibrium between the free  $\text{F}^-$  ion and the addition product was fast on NMR time scale. On addition of 0.25 equivalent of  $\text{F}^-$  ion, the doublet at -23.5 ppm disappeared and two broad peaks were observed which disappeared completely on addition of 0.5 equivalent of  $\text{F}^-$  ion. It clearly indicated that the  $\text{F}^-$  ion was now exchanging rapidly with the pentavalent Si-F fluorine, in addition to the four coordinate Si-F fluorine. As the concentration of  $\text{F}^-$  ion was increased the four coordinate silicon atom moved more towards high field showing that the tetravalent silicon atom was becoming more pentavalent. At 1 equivalent of  $\text{F}^-$  ion, two broad signals were observed in silicon-29 NMR. The peak at -74.2 ppm was due to four coordinate silicon atom which became pentavalent on addition of  $\text{Bu}_4\text{N}^+\text{F}^-$ , and the peak at -25.2 ppm was due



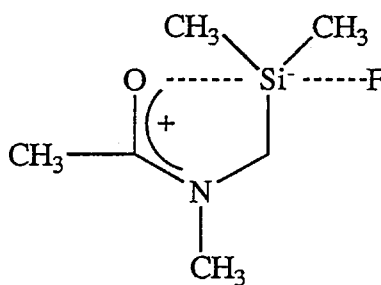
Scheme 3.12 Interaction between bis(fluorodimethylsilylmethyl)acetamide (4.8)  
and tetrabutylammoniumfluoride



to the pentavalent silicon atom coordinated to oxygen (Table 3.8). Although the position of the pentavalent silicon atom had hardly moved at all, the lack of Si-F coupling constant was an indication of equilibrium between free  $F^-$  ion and Si-F bond (Scheme 3.12).

#### Reaction of fluorodimethylsilylmethyl-N-methylacetamide (3.13) with NMI

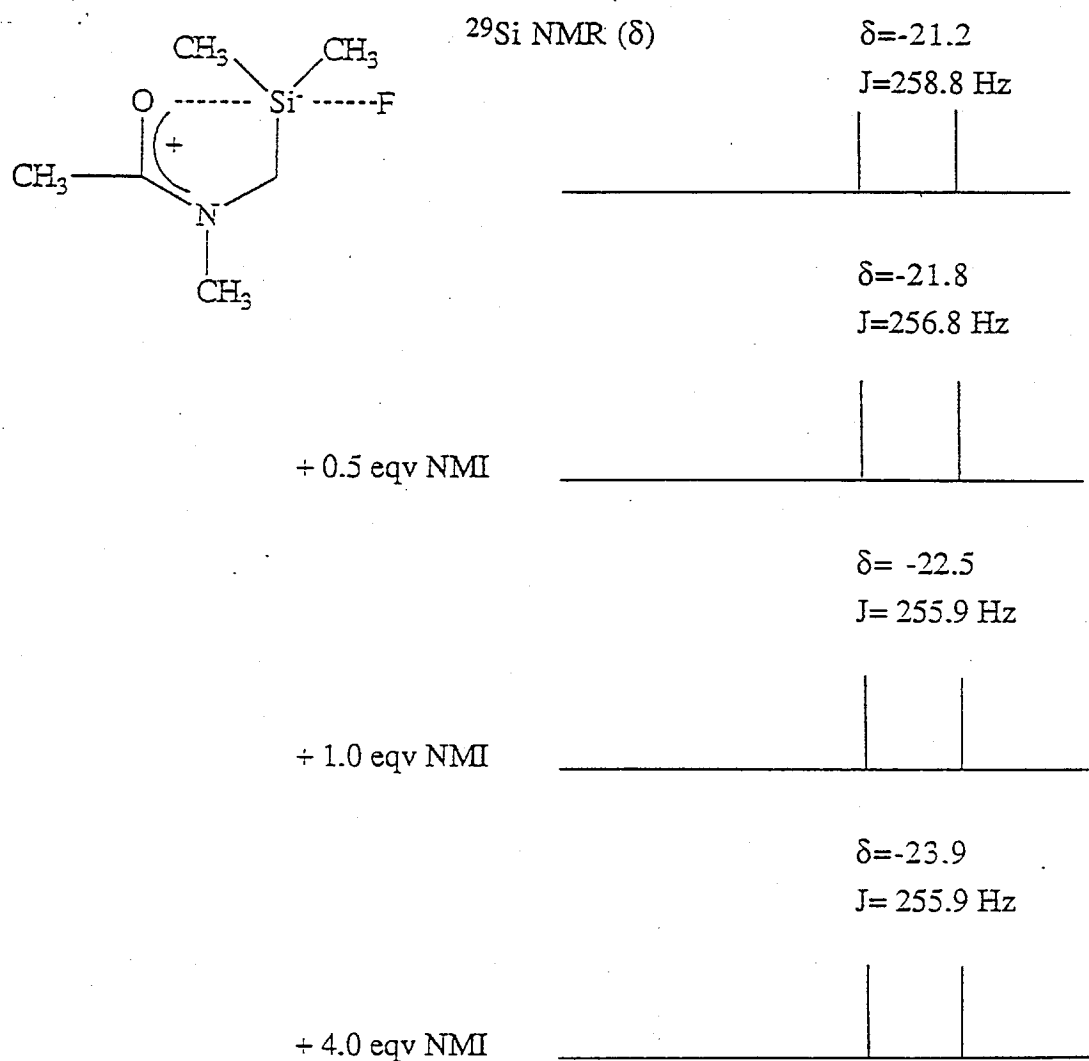
We found that the five coordinate silicon atom of silyl fluoride (3.8) was unreactive towards nucleophiles. The result was quite unexpected and to prove this result further, we have decided to treat NMI with fluorodimethylsilylmethyl-N-methylacetamide (3.13). We observed that the five coordinate silicon atom was unreactive even in presence of excess NMI (Scheme 3.13). The Si-F coupling constant was maintained throughout the process of addition. The results are shown in Table 3.9.



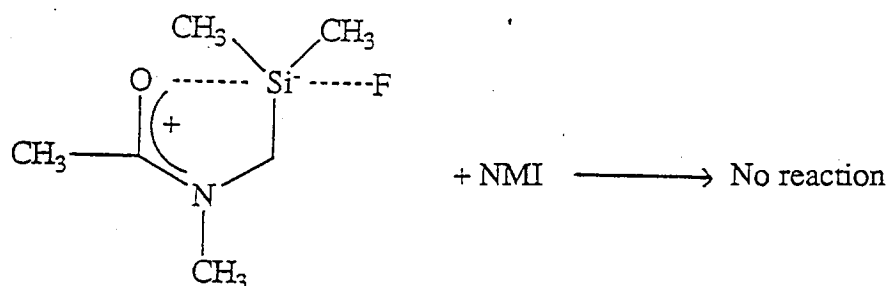
(3.13)

As we have mentioned in introduction of this chapter a lot of work has been done on the reactivity of tetra- and hypervalent silicon compounds. Each system behaves quite differently towards a particular nucleophilic reagent. We found in our study that, when chloro and bromo-bis silyl amide were treated with nucleophiles, e.g., NMI, HMPA substitution took place exclusively at the pentavalent silicon atom. Similar results were obtained by Corriu and coworkers<sup>89,107</sup>. They have

Scheme 3.13 Interaction between fluorodimethylsilylmethyl-N-methyl acetamide (3.13) and NMI

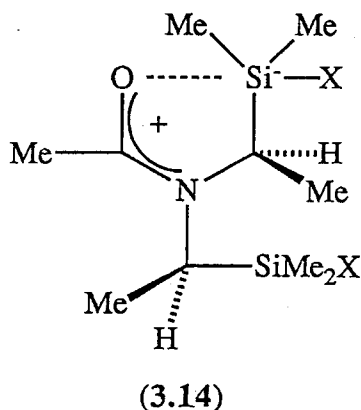


No line broadening even with a large excess of NMI



shown that five coordinate silicon atom was more reactive than the four coordinate silicon both thermodynamically and kinetically<sup>89,107</sup>. But our results were opposite to that of Corriu, when fluoro-bis silyl amide was treated with nucleophiles. Instead of five, substitution took place at the four coordinate silicon.

We could not give any firm conclusion about which silicon atom was kinetically more reactive. The tetravalent silicon could possibly be kinetically but not thermodynamically more reactive than the five coordinate silicon. We tried to probe this effect by making the compound (3.14).



The  $\text{SiMe}_2$  groups in (3.14) would be diastereotopic. Our assumption was that, if the four coordinate silicon reacts faster than the five coordinate silicon kinetically, then addition of a catalytic amount of NMI will collapse the diastereotopicity at silicon and the doublet will appear as a singlet. Similar result was obtained by Lau<sup>149</sup>, when catalytic amount of NMI was added to  $\text{PhCHMeSiMe}_2\text{Cl}$ . But we were unable to prepare the compound (3.14), so we were unable to compare the kinetic reactivity between four and five coordinate silicon atoms. So, the results described in this part of the thesis were based on the basis of thermodynamic reactivity of four and five coordinate silicons.

We observed that when 0.5 equivalent of NMI was added to bis-silyl chloride (3.7, X=Cl), substitution took place at the pentavalent silicon atom. The position of the four coordinate silicon in silicon-29 NMR was unaffected in the presence of 1 equivalent of NMI (Table 3.3). The possible explanations for high reactivity of five coordinated bis-silyl chloride could be a longer Si-Cl bond in a "semi ionic" state due to the high polarisability of the chlorine atom, as observed recently in some pentacoordinated structures<sup>42,60,127</sup> or it may be due to a weakly bound ligand (Cl) opposite to a strongly bound ligand (O), where the more strongly bound ligand oxygen pushes the weakly bound ligand chlorine away and makes the Si-Cl bond weaker than the normal Si-Cl bond<sup>128</sup>. In addition, it has been shown that the Si-Cl bond can be stretched by approximately 17%<sup>129</sup>. Similar results were obtained when bis-silyl bromide (3.7, X=Br) was treated with NMI and a similar explanations can be put forward for its reactivity.

The reactivity of homosubstituted bis-silylamide halo derivatives have shown quite interesting results towards different nucleophiles. For example, the five coordinated silyl chloride and bromide were found to be more reactive than the four coordinated silyl chloride and bromide, but the four coordinated silyl fluoride was found to be more reactive than the five coordinated silyl fluoride. Having finished the reactivity of homosubstituted bis-silylamide halo derivatives, we have decided to study the reactivity of heterosubstituted bis-silylamide halo derivatives towards different nucleophilic reagents. It was observed that, the five coordinated silicon was always found to be more reactive than the four coordinated silicon and the results are discussed below.

### Reaction of chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) with NMI

Substitution took place at the pentacoordinate silicon when 0.5 equivalent of NMI was added to (3.9). A broad peak at -38.1 ppm showed the complex to be in equilibrium between 3.2A and 3.2B due to nucleophilic attack by the chloride ion at

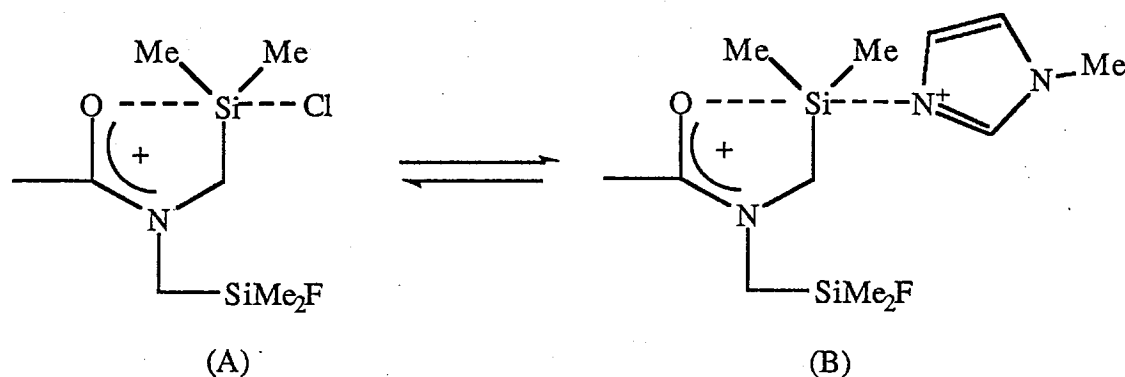


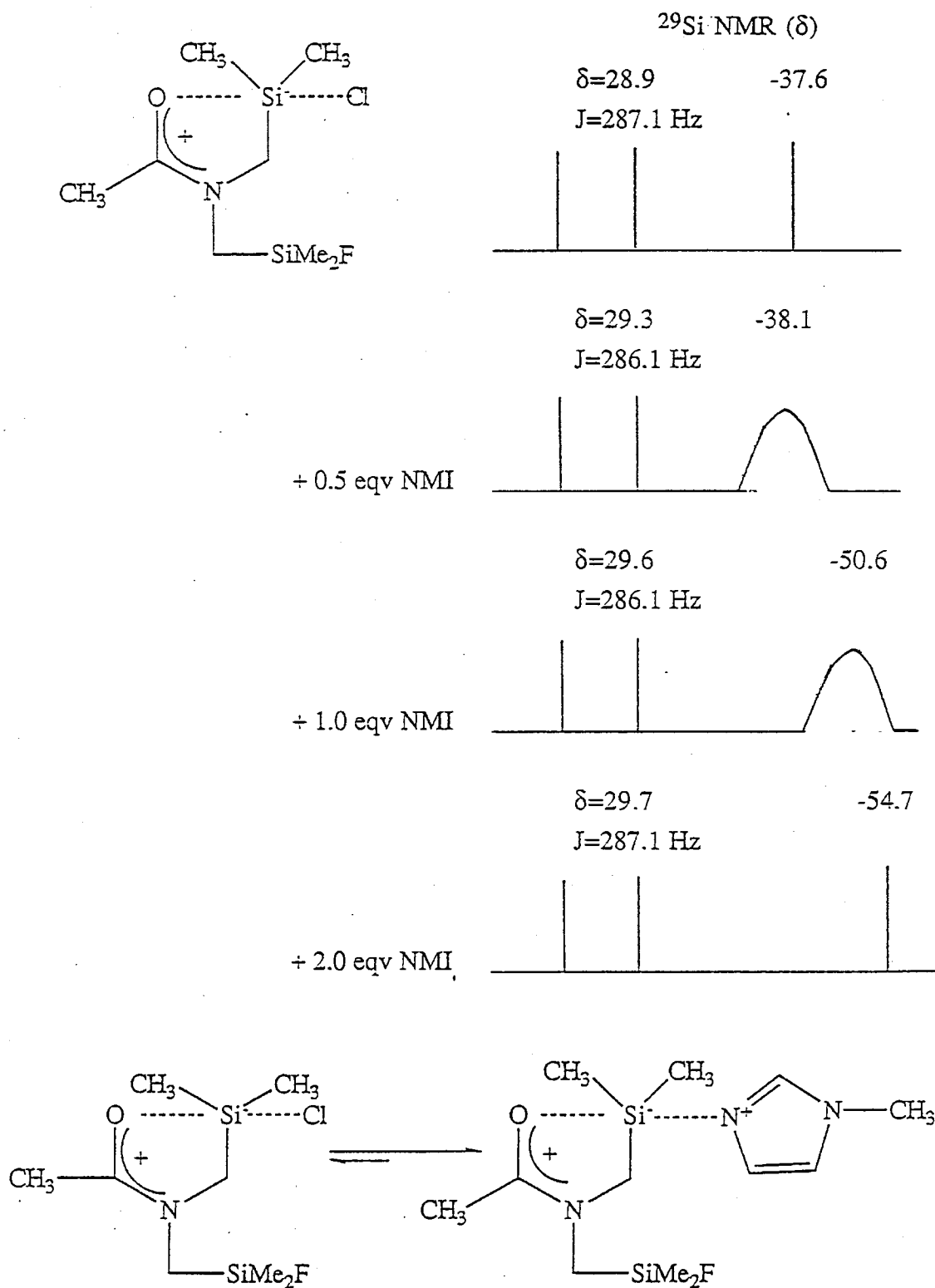
Figure 3.2

the silicon atom of the substitution product. Shifting of silicon-29 peak from -37.6 ppm to -50.6 ppm on addition of 1 equivalent of NMI reflected the almost complete conversion to the substitution product which is thermodynamically favoured (Scheme 3.14). That the excess of NMI gave substitution product was confirmed by a sharp signal in silicon-29 NMR at -54.7 ppm (Scheme 3.14) (Table 3.1), together with increased deshielding of the NMI in proton resonance, particularly at C-2 position, confirmed the formation of the dative Si-N bond. The tetracoordinated silicon was unaffected even in the presence of excess NMI.

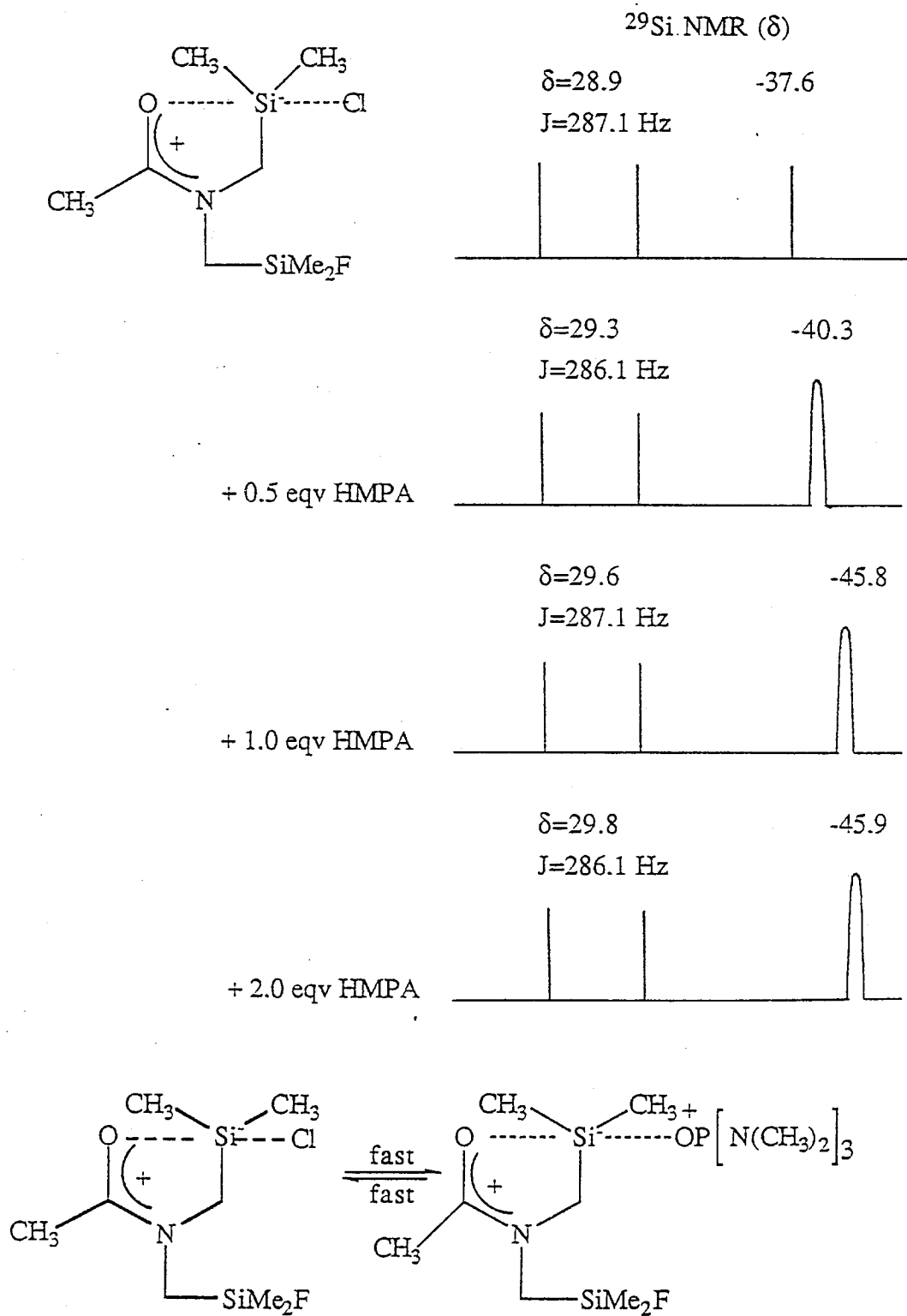
### Reaction of chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) with HMPA

We found a similar result to that for NMI when HMPA was added to chlorofluorobis(dimethylsilylmethyl)acetamide (3.9). Like NMI, HMPA attacked

Scheme 3.14 Interaction between chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) and NMI



Scheme 3.15 Interaction between chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) and HMPA





the pentacoordinate silicon atom and gave the substitution product (Table 3.10). Again the lack of the Si-P coupling is because the back reaction is fast even if the equilibrium lies to the right (Scheme 3.15).

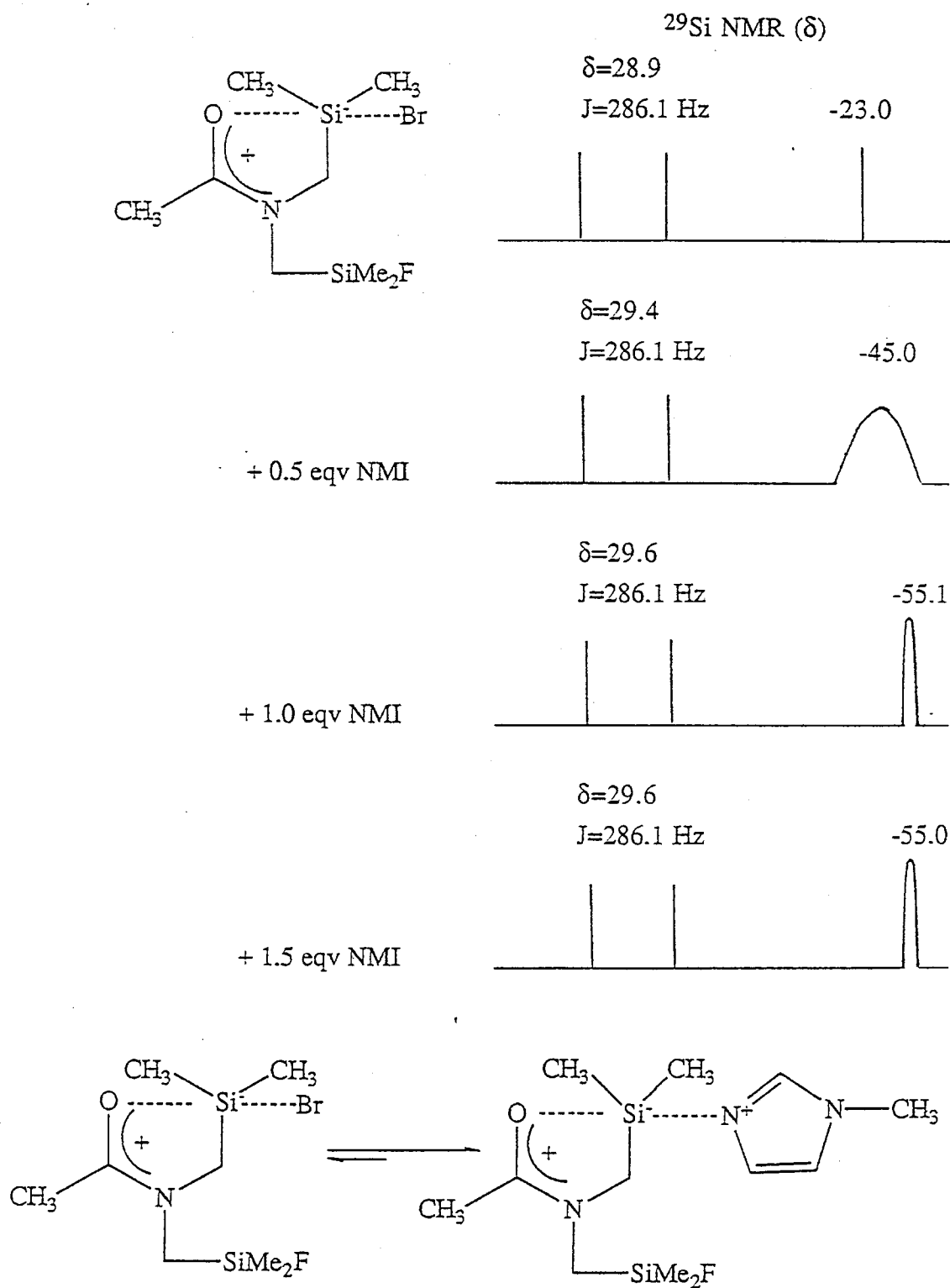
#### Reaction of bromofluorobis(dimethylsilylmethyl)acetamide (3.10) with NMI

Substitution took place at the pentavalent silicon atom as expected, when NMI was added to bromofluorobis(dimethylsilylmethyl)acetamide (3.10). A gradual upfield shift of the silicon-29 NMR was observed as the concentration of NMI increased, indicating that the equilibrium lies more towards substitution (Scheme 3.16). The downfield shift of NMI in proton spectra confirmed the complexation of NMI with the silicon atom (Table 3.2).

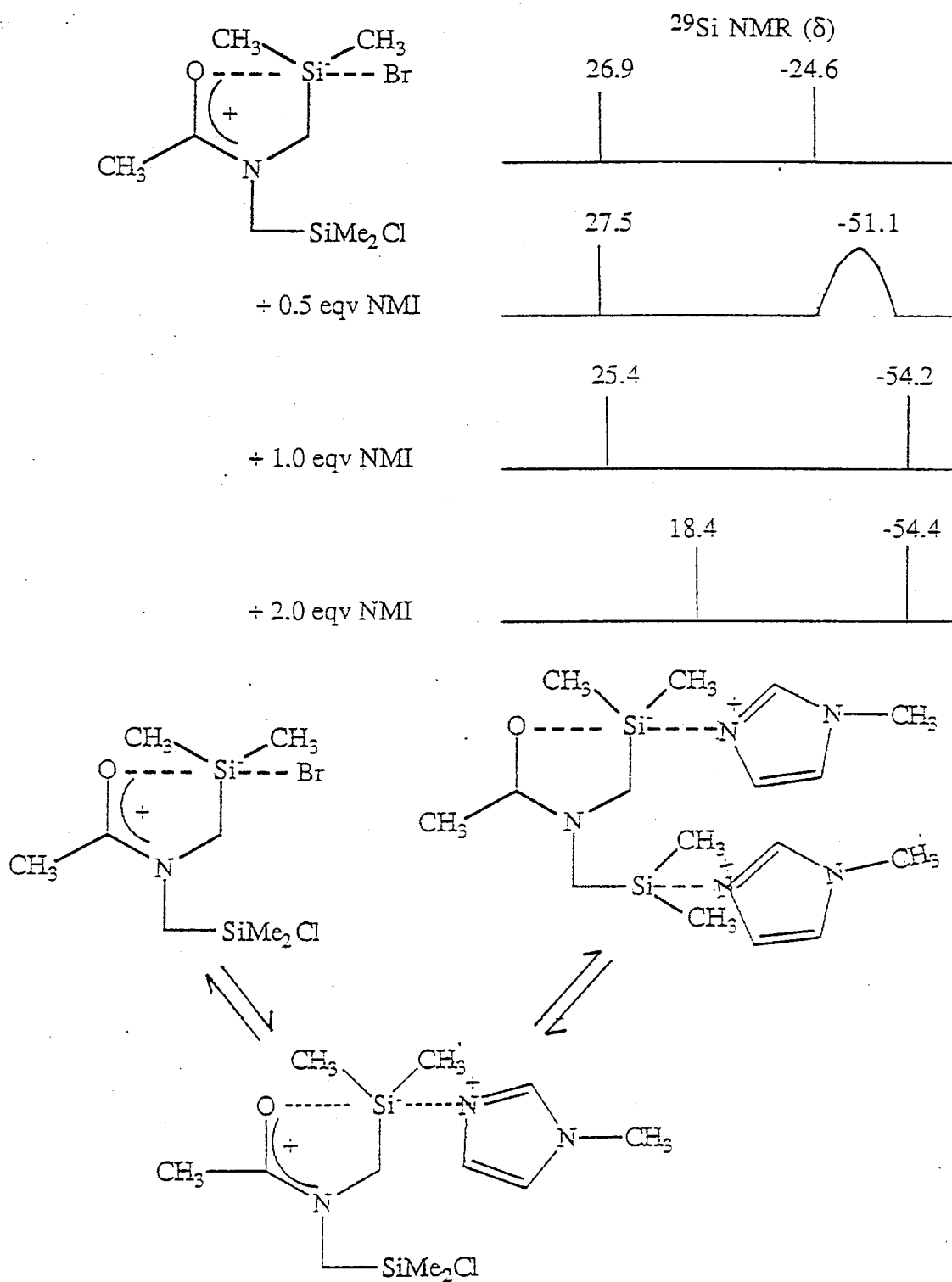
#### Reaction of bromochlorobis(dimethylsilylmethyl)acetamide (3.11) with NMI

We observed the expected behaviour when NMI was added to bromochlorobis(dimethylsilylmethyl)acetamide (3.11). The peak at -24.6 ppm observed in silicon-29 NMR before addition of NMI moved to -54.2 ppm on addition of 1 equivalent of NMI. It clearly showed that the substitution was taking place at the pentacoordinate silicon. The down field shift of NMI in proton NMR proved the formation of a dative Si-N bond (Table 3.11). The peak assigned for the tetravalent silicon moved to about 8 ppm upfield on addition of 2 equivalents of NMI. It clearly showed that some substitution was taking place at the tetravalent silicon (Scheme 3.17) as was observed for 3.7 (X=Cl).

Scheme 3.16 Interaction between bromofluorobis(dimethylsilylmethyl)acetamide (3.10) and NMI



Scheme 3.17 Interaction between bromochlorobis(dimethylsilylmethyl)acetamide (3.11) and NMI

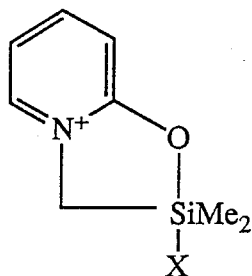


### 3.3 CONCLUSIONS AND SUMMARY:

The enhanced reactivity of pentavalent species, compared to tetravalent silicon has also been suggested by calculations<sup>150</sup> which showed that only a small change in charge occurred at silicon on going from the tetravalent to the pentavalent anionic species. However, a general loosening of all bonds in the pentacoordinate state occurred, and hence the enhanced reactivity was associated with a greater leaving group ability on going from tetra- to pentacoordinated species.

We observed an unexpected result when silyl fluoride (3.8) was treated with nucleophiles. Substitution took place at the four coordinate silicon instead of five. This unexpected behaviour was difficult to explain, but the most probable explanations could be put forward on the basis of our previous results observed on pyridone system.

(a) Our previous result has shown that the compound (3.15) was truly pentacoordinate whereas the compound (3.16) was more tetra than



(3.15) X=Cl

(3.16) X=F

pentacoordinate. Perhaps this has made the Si-F bond less reactive in some way; possibly by 'tightening' the Si-F bond.

(b) Fluoride ion activates tetracoordinate silicon-fluoride, but not the pentavalent Si-F bond.

The greater reactivity of four coordinate silicon atom was lost when the fluorine atom attached to five coordinate silicon was replaced either by chlorine or bromine. So, addition of NMI or HMPA to (3.9) or (3.10) gave the substitution product exclusively at the pentacoordinate silicon.

The four coordinate Si-F coupling collapsed on addition of catalytic amount of  $\text{Bu}_4\text{N}^+\text{F}^-$  to 3.8. It showed that  $\text{F}^-$  ion attacks the four coordinate silicon. But the five coordinate Si-F coupling constant starts collapsing as the amount of  $\text{F}^-$  ion was increased. The mechanism of  $\text{F}^-$  ion exchange has not been fully understood. The most probable mechanism was shown in Scheme 3.12.

In conclusion, the comparison between four and five coordinated silicon species showed that the latter were more reactive towards nucleophilic substitution (except the bis-fluoro amide 3.8, where four coordinate silicon atom was found to be more reactive). The enhanced reactivity observed was also suggested by calculations<sup>150</sup> which showed that in pentacoordinated anionic species there was only a small change in charge at silicon; however, a general loosening of all bonds in the pentacoordinated states occurred, which showed that the enhanced reactivity of the pentavalent silicon was associated with a greater leaving group ability on going from four to five coordinate species<sup>150</sup>.

The work described in this section is the first where investigations of five versus four coordinated silicon atom have been carried out under controlled conditions and even if some results were not absolutely clear-cut at least the situation is in a position to be resolved more readily than ever before.

**Table 3.1** Interaction between chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (3.9) : NMI				
		1:0	1:0.5	1:1	1:2	0:1
$^1\text{H}$	H-2	-	9.2	9.3	9.0	7.4
	H-4	-	7.6	7.7	7.6	7.0
	H-5	-	7.2	7.2	7.2	6.9
	NCH <sub>3</sub>	-	4.1	4.1	4.0	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.41 d	0.40 d	0.31 d	0.30 d	-
	$^3J_{\text{HF}}$	7.6 Hz	7.6 Hz	7.3 Hz	7.2 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	0.51	0.50	0.43	0.47	-
	COCH <sub>3</sub>	2.2	2.2	2.2	2.3	-
	CH <sub>2</sub> Si <sup>a</sup>	3.2 d	3.4 d	3.4 d	3.4 d	-
	$^3J_{\text{HF}}$	6.6 Hz	6.6 Hz	6.6 Hz	6.5 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	2.8	2.8	2.8	2.9	-
$^{13}\text{C}$	C-2	-	137.6 (sbr)	137.8 (sbr)	137.9 (sbr)	137.8
	C-4	-	122.7	122.6 (sbr)	124.1	129.5
	C-5	-	122.7	122.6 (sbr)	122.0	120.1
	NCH <sub>3</sub>	-	35.3	34.9	34.3	-
	CH <sub>3</sub> Si <sup>a</sup>	-1.9 d	-1.8 d	-2.1 d	-2.1 d	-
	$^2J_{\text{CF}}$	14.2 Hz	14.2 Hz	14.2 Hz	13.0 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	6.6	5.2	3.4	2.2	-
	COCH <sub>3</sub>	17.4	17.5	17.2	17.2	-
	CO	172.8	172.9	172.7	173.1	-
	CH <sub>2</sub> Si <sup>a</sup>	41.3 d	41.4 d	41.2 d	41.9 d	-
	$^2J_{\text{CF}}$	15.5 Hz	15.5 Hz	15.5 Hz	15.5 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	44.2	43.0	40.2	40.9	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	28.9 d	29.3 d	29.6 d	29.7 d	-
	$^1J_{\text{SiF}}$	287.1 Hz	286.1 Hz	286.1 Hz	287.1 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	-37.6	-38.1 (br)	-50.6 (br)	-54.7	-

Quantities used:

(3.9) (mmol)            2            2            2            2            -

NMI (mmol)            -            1            2            4            2

Solvent : CDCl<sub>3</sub>, 2 ml

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

**Table 3.2** Interaction between bromofluorobis(dimethylsilylmethyl)acetamide(**3.10**) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of ( <b>3.10</b> ) : NMI				
		1:0	1:0.5	1:1	1:1.5	0:1
$^1\text{H}$	H-2	-	9.2	9.0	8.6	7.4
	H-4	-	7.6	7.5	7.4	7.0
	H-5	-	7.2	7.2	7.2	6.9
	NCH <sub>3</sub>	-	4.1	4.0	3.9	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.45 d	0.41 d	0.41 d	0.33 d	-
	$^3\text{J}_{\text{HF}}$	6.3 Hz	6.3 Hz	6.3 Hz	8.6 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	0.65	0.46	0.46	0.46	-
	COCH <sub>3</sub>	2.3	2.2	2.3	2.2	-
	CH <sub>2</sub> Si <sup>a</sup>	3.3 d	3.3 d	3.4 d	3.3 d	-
	$^3\text{J}_{\text{HF}}$	5.9 Hz	5.9 Hz	5.9 Hz	5.9 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	3.0	2.8	2.7	2.9	-
$^{13}\text{C}$	C-2	-	136.8	136.8	137.0	137.8
	C-4	-	122.9	123.3	124.7	129.5
	C-5	-	122.2	121.9	121.4	120.1
	NCH <sub>3</sub>	-	35.2	34.6	34.1	33.3
	CH <sub>3</sub> Si <sup>a</sup>	-1.7 d	-1.7 d	-2.1 d	-2.1 d	-
	$^2\text{J}_{\text{CF}}$	14.2 Hz	14.2 Hz	14.2 Hz	14.2 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	6.4	3.9	2.0	2.2	-
	COCH <sub>3</sub>	17.6	17.7	17.6	17.4	-
	CO	173.7	172.9	172.3	172.8	-
	CH <sub>2</sub> Si <sup>a</sup>	41.9 d	41.3 d	41.9 d	42.0 d	-
	$^2\text{J}_{\text{CF}}$	15.5 Hz	19.4 Hz	15.5 Hz	16.8 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	45.6	41.3	40.8	40.8	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	28.9 d	29.4 d	29.6 d	29.6 d	-
	$^1\text{J}_{\text{SiF}}$	286.1 Hz	286.1 Hz	286.1 Hz	286.1 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	-23.0	-45.0 (br)	-55.1 (sbr)	-55.0 (sbr)	-

Quantities used:

(**3.10**) (mmol)      2      2      2      2      -  
 NMI (mmol)      -      1      2      3      2

Solvent : CDCl<sub>3</sub>, 2 ml

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom



**Table 3.3 Interaction between bis(chlorodimethylsilylmethyl)acetamide(3.7,X=Cl) and N-methylimidazole (NMI): NMR Data**

$\delta$ (ppm)		Ratio of (3.7,X=Cl) : NMI				
		1:0	1:0.5	1:1	1:2	0:1
$^1\text{H}$	H-2	-	9.0	9.2	8.5	7.4
	H-4	-	7.5	7.7	7.3	7.0
	H-5	-	7.1	7.5	7.2	6.9
	N-CH <sub>3</sub>	-	4.0	4.3	3.9	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.56	0.59	0.80	0.60	-
	CH <sub>3</sub> Si <sup>b</sup>	0.61	0.62	1.0	0.85	-
	COCH <sub>3</sub>	2.2	2.3	2.6	2.3	-
	CH <sub>2</sub> Si <sup>a</sup>	3.3	3.5	3.9	2.9	-
	CH <sub>2</sub> Si <sup>b</sup>	2.8	2.9	3.1	3.7	-
$^{13}\text{C}$	C-2	-	137.4	138.4	138.4	137.8
	C-4	-	123.0	124.9	126.6	129.5
	C-5	-	122.3	121.8	121.8	120.1
	N-CH <sub>3</sub>	-	32.1	34.8	34.2	33.3
	CH <sub>3</sub> Si <sup>a</sup>	1.9	1.7	1.5	0.40	-
	CH <sub>3</sub> Si <sup>b</sup>	7.4	4.5	2.6	2.5	-
	COCH <sub>3</sub>	17.6	17.4	17.7	17.8	-
	CO	173.1	173.0	173.6	173.9	-
	CH <sub>2</sub> Si <sup>a</sup>	42.6	35.0	41.2	40.9	-
	CH <sub>2</sub> Si <sup>b</sup>	44.6	42.5	42.5	42.1	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	26.8	27.2	26.0	19.1	-
	CH <sub>3</sub> Si <sup>b</sup>	-39.9	null signal		-53.9 (sbr)	-54.4

Quantities used:

(3.7,X=Cl)(mmol)	2	2	2	2	-
NMI (mmol)	--	1	2	4	2

Solvent: CDCl<sub>3</sub>, 2ml

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

Table 3.4 Interaction between bis(chlorodimethylsilylmethyl)acetamide(3.7,X=Cl) and hexamethylphosphoramide (HMPA): NMR Data

$\delta$ (ppm)		Ratio of (3.7,X=Cl) : HMPA				
		1:0	1:0.5	1:1	1:1.5	0:1
$^1\text{H}$	N-CH <sub>3</sub>	-	2.7 d	2.7 d	2.6 d	2.8d
	$^3\text{J}_{\text{PH}}$		9.8 Hz	9.3 Hz	9.3 Hz	9.3 Hz
	CH <sub>3</sub> Si <sup>a</sup>	0.56	0.44	0.39	0.38	-
	CH <sub>3</sub> Si <sup>b</sup>	0.61	0.66	0.68	0.67	-
	COCH <sub>3</sub>	2.2	2.3	2.6	2.3	-
	CH <sub>2</sub> Si <sup>a</sup>	3.3	3.6	3.7	3.8	-
	CH <sub>2</sub> Si <sup>b</sup>	2.8	3.2	3.2	3.2	-
$^{13}\text{C}$	N-CH <sub>3</sub>	--	36.3 d	36.2 d	36.2 d	36.7 d
	$^2\text{J}_{\text{PC}}$	--	3.9 Hz	3.9 Hz	3.9 Hz	3.9 Hz
	CH <sub>3</sub> Si <sup>a</sup>	1.9	1.6	1.6	1.6	-
	CH <sub>3</sub> Si <sup>b</sup>	7.4	5.4	4.7	4.8	-
	COCH <sub>3</sub>	17.6	17.5	17.5	17.5	-
	CO	173.1	173.0	173.0	173.1	-
	CH <sub>2</sub> Si <sup>a</sup>	42.6	42.2	42.1	42.1	-
	CH <sub>2</sub> Si <sup>b</sup>	44.6	42.2	42.1	42.1	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	26.8	27.8	28.0	28.0	-
	CH <sub>3</sub> Si <sup>b</sup>	-39.9	-43.9 (sbr)	-45.5 (sbr)	-45.9 (sbr)	-
Quantities used:						
(3.7,X=Cl)(mmol)		2	2	2	2	--
HMPA (mmol)		--	1	2	3	2
Solvent: CDCl <sub>3</sub> , 2ml						

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

**Table 3.5 Interaction between bis(bromodimethylsilylmethyl)acetamide (3.7, X=Br) and N-methylimidazole (NMI): NMR Data**

$\delta$ (ppm)		Ratio of (3.7,X=Br) : NMI				
		1:0	1:0.5	1:1	1:1.5	0:1
$^1\text{H}$	H-2	-	9.2	9.3	9.3	7.4
	H-4	-	7.6	7.7	7.7	7.0
	H-5	-	7.2	7.3	7.4	6.9
	NCH <sub>3</sub>	-	4.1	4.1	4.1	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.73	0.66	0.58	0.58	-
	CH <sub>3</sub> Si <sup>b</sup>	0.83	0.71	0.72	0.86	-
	COCH <sub>3</sub>	2.3	2.4	2.4	2.4	-
	CH <sub>2</sub> Si <sup>a</sup>	3.6	3.6	3.7	3.9	-
	CH <sub>2</sub> Si <sup>b</sup>	3.2	3.1	2.9	2.9	-
$^{13}\text{C}$	C-2	-	136.6	136.7	137.1	137.8
	C-4	-	122.5	122.5	122.7	129.5
	C-5	-	121.3	121.0	121.0	120.1
	NCH <sub>3</sub>	-	35.3	35.0	34.8	33.3
	CH <sub>3</sub> Si <sup>a</sup>	2.4	2.0	1.4	0.63	-
	CH <sub>3</sub> Si <sup>b</sup>	6.8	4.7 (sbr)	2.4 (sbr)	2.0	-
	COCH <sub>3</sub>	17.9	17.6	17.5	17.4	-
	CO	174.6	173.7	173.0	173.3	-
	CH <sub>2</sub> Si <sup>a</sup>	43.0	42.6	40.8	40.6	-
	CH <sub>2</sub> Si <sup>b</sup>	46.4	43.0 (sbr)	42.2	41.5	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	26.0	26.8	27.3	24.3	-
	CH <sub>3</sub> Si <sup>b</sup>	-13.8	null signal	-52.8 (sbr)	-54.1	-
Quantities used:						
(3.7,X=Br)(mmol)	2	2	2	2	--	
NMI (mmol)	--	1	2	3	2	
Solvent: CDCl <sub>3</sub> , 2ml						

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

Table 3.6 Interaction between bis(fluorodimethylsilylmethyl)acetamide (3.8) and N-methylimidazole (NMI): NMR Data

$\delta$ (ppm)		Ratio of (3.8) : NMI				
		1:0	1:0.5	1:1	1:1.5	0:1
$^1\text{H}$	H-2	--	7.4	7.4	7.4	7.4
	H-4	--	7.0	7.0	7.0	7.0
	H-5	--	6.9	6.9	6.9	6.9
	NCH <sub>3</sub>	--	3.7	3.7	3.6	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.23d	0.18	0.18	0.18	--
	$^3J_{\text{HF}}$	7.6 Hz	--	--	--	--
	CH <sub>3</sub> Si <sup>b</sup>	0.37d	0.32d	0.31d	0.30d	--
	$^3J_{\text{HF}}$	7.6 Hz	8.3 Hz	7.8 Hz	7.3 Hz	--
	COCH <sub>3</sub>	2.1	2.1	2.0	2.0	--
	CH <sub>2</sub> Si <sup>a</sup>	3.1d	3.1	3.1	3.1	--
	$^3J_{\text{HF}}$	6.6 Hz	--	--	--	--
	CH <sub>2</sub> Si <sup>b</sup>	2.4	2.4	2.4	2.4	--
$^{13}\text{C}$	C-2	--	137.7	137.4	137.4	137.8
	C-4	--	129.2	128.8	128.7	129.5
	C-5	--	120.2	119.8	119.8	120.1
	NCH <sub>3</sub>	--	33.2	32.8	32.7	33.3
	CH <sub>3</sub> Si <sup>a</sup>	-1.8d	-1.8	-1.9	-1.9	--
	$^2J_{\text{CF}}$	14.2 Hz	--	--	--	--
	CH <sub>3</sub> Si <sup>b</sup>	1.8d	1.9d	1.9d	1.9d	--
	$^2J_{\text{CF}}$	24.6 Hz	24.6 Hz	25.9 Hz	24.6 Hz	--
	COCH <sub>3</sub>	18.3	18.2	17.8	17.8	--
	CO	171.2	171.2	170.9	170.9	--
	CH <sub>2</sub> Si <sup>a</sup>	39.4	39.3	38.9	38.9	--
	CH <sub>2</sub> Si <sup>b</sup>	41.7d	41.4	41.0	41.0	--
	$^2J_{\text{CF}}$	18.1 Hz	10.4 Hz	10.4 Hz	10.4 Hz	--
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	28.9 d	null signal	30 (br)	30 (br)	--
	$^1J_{\text{SiF}}$	287.1 Hz	--	--	--	--
	CH <sub>3</sub> Si <sup>b</sup>	-23.5 d	-24.0 d	-24.5 d	-24.9 d	--
	$^1J_{\text{SiF}}$	256.8 Hz	256.8 Hz	255.9 Hz	255.8 Hz	--

Quantities used:

(3.8) (mmol)	2	2	2	2	--
NMI (mmol)	--	1	2	3	2
Solvent: CDCl <sub>3</sub> , 2ml					

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

**Table 3.7** Interaction between bis(fluorodimethylsilylmethyl)acetamide (3.8) and hexamethylphosphoramide (HMPA): NMR Data

$\delta$ (ppm)		Ratio of (3.8) : HMPA				
		1:0	1:0.5	1:1	1:2	0:1
$^1\text{H}$	NCH <sub>3</sub>	-	2.7 d	2.7 d	2.6 d	2.8 d
	$^3\text{J}_{\text{PH}}$		9.3 Hz	9.3 Hz	9.4 Hz	9.3 Hz
	CH <sub>3</sub> Si <sup>a</sup>	0.23 d	0.37	0.38	0.37	-
	$^3\text{J}_{\text{HF}}$	7.6 Hz	-	-	-	-
	CH <sub>3</sub> Si <sup>b</sup>	0.37 d	0.31 d	0.31 d	0.19 d	-
	$^3\text{J}_{\text{HF}}$	7.6 Hz	7.8 Hz	7.8 Hz	7.6 Hz	-
	COCH <sub>3</sub>	2.1	2.1	2.1	2.1	-
	CH <sub>2</sub> Si <sup>a</sup>	3.1 d	3.1	3.1	3.1	-
	$^3\text{J}_{\text{HF}}$	6.6 Hz	-	-	-	-
	CH <sub>2</sub> Si <sup>b</sup>	2.4	2.4	2.4	2.4	-
$^{13}\text{C}$	NCH <sub>3</sub>	-	36.8 d	36.8 d	36.7 d	36.7 d
	$^2\text{J}_{\text{PC}}$		3.9 Hz	3.9 Hz	3.9 Hz	3.9 Hz
	CH <sub>3</sub> Si <sup>a</sup>	-1.8 d	-1.8	-1.8	-1.9	-
	$^2\text{J}_{\text{CF}}$	14.2 Hz	-	-	-	-
	CH <sub>3</sub> Si <sup>b</sup>	1.8 d	1.8 d	1.9 d	1.2 d	-
	$^2\text{J}_{\text{CF}}$	24.6 Hz	24.6 Hz	24.6 Hz	25.9 Hz	-
	COCH <sub>3</sub>	18.3	18.2	18.2	18.2	-
	CO	171.2	171.2	171.3	171.2	-
	CH <sub>2</sub> Si <sup>a</sup>	39.4	39.3	39.3	39.2	-
	CH <sub>2</sub> Si <sup>b</sup>	41.7 d	41.4 d	41.4 d	41.3	-
	$^2\text{J}_{\text{CF}}$	18.1 Hz	11.7 Hz	11.7 Hz	10.4 Hz	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	28.9 d	null signal	30.9 (br)	29.1 (br)	-
	$^1\text{J}_{\text{SiF}}$	287.1 Hz	-	-	-	-
	CH <sub>3</sub> Si <sup>b</sup>	-23.5 d	-24.0 d	-24.5 d	-25.2 d	-
	$^1\text{J}_{\text{SiF}}$	256.8 Hz	255.9 Hz	255.9 Hz	256.8 Hz	-

Quantities used:

(3.8) (mmol)	2	2	2	2	-
HMPA (mmol)	-	1	2	4	2
Solvent : CDCl <sub>3</sub> , 2ml					

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom





**Table 3.10** Interaction between chlorofluorobis(dimethylsilylmethyl)acetamide (3.9) and hexamethylphosphoramide (HMPA) : NMR Data

$\delta$ (ppm)		Ratio of (3.9) : HMPA				
		1:0	1:0.5	1:1	1:2	0:1
$^1\text{H}$	NCH <sub>3</sub>	-	2.7 d	2.7 d	2.7 d	2.8 d
	$^3\text{J}_{\text{PH}}$		9.8 Hz	9.3 Hz	9.8 Hz	9.3 Hz
	CH <sub>3</sub> Si <sup>a</sup>	0.41 d	0.35 d	0.33 d	0.31 d	-
	$^3\text{J}_{\text{HF}}$	7.6 Hz	6.1 Hz	6.0 Hz	6.0 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	0.51	0.46	0.40	0.39	-
	COCH <sub>3</sub>	2.2	2.2	2.3	2.3	-
	CH <sub>2</sub> Si <sup>a</sup>	3.2 d	3.3 d	3.5 d	3.4 d	-
	$^3\text{J}_{\text{HF}}$	6.6 Hz	7.1 Hz	7.1 Hz	7.0 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	2.8	3.1	3.2	3.3	-
$^{13}\text{C}$	NCH <sub>3</sub>	-	36.7 d	36.7 d	36.7 d	-
	$^2\text{J}_{\text{PC}}$	-	5.2 Hz	3.9 Hz	3.9 Hz	3.9 Hz
	CH <sub>3</sub> Si <sup>a</sup>	-1.9 d	-1.8 d	-1.8 d	-1.9 d	-
	$^2\text{J}_{\text{CF}}$	14.2 Hz	14.2 Hz	14.2 Hz	14.2 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	6.6	5.5	4.8	4.4	-
	COCH <sub>3</sub>	17.4	17.7	17.7	17.7	-
	CO	172.8	173.0	173.1	173.1	-
	CH <sub>2</sub> Si <sup>a</sup>	41.3 d	41.5 d	41.5 d	41.5 d	-
	$^2\text{J}_{\text{CF}}$	15.5 Hz	15.5 Hz	14.2 Hz	15.5 Hz	-
	CH <sub>2</sub> Si <sup>b</sup>	44.2	43.1	42.5	42.5	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	28.9 d	29.3 d	29.6 d	29.8 d	-
	$^1\text{J}_{\text{SiF}}$	287.1 Hz	286.1 Hz	287.1 Hz	286.1 Hz	-
	CH <sub>3</sub> Si <sup>b</sup>	-37.6	-40.3 (sbr)	-45.8 (sbr)	-45.9 (sbr)	-
Quantities used:						
(3.9) (mmol)		2	2	2	2	-
HMPA (mmol)		-	1	2	4	2
Solvent : CDCl <sub>3</sub> , 2 ml						

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom



**Table 3.11** Interaction between bromochlorobis(dimethylsilylmethyl)acetamide (3.11) and N-methylimidazole (NMI) : NMR Data

$\delta$ (ppm)		Ratio of (3.11) : NMI				
		1:0	1:0.5	1:1	1:2	0:1
$^1\text{H}$	H-2	-	9.2	8.7	8.4	7.4
	H-4	-	7.6	7.3	7.2	7.0
	H-5	-	7.2	7.1	7.0	6.9
	NCH <sub>3</sub>	-	4.1	3.7	3.7	3.7
	CH <sub>3</sub> Si <sup>a</sup>	0.66	0.57	0.30	0.29	-
	CH <sub>3</sub> Si <sup>b</sup>	0.68	0.67	0.62	0.64	-
	COCH <sub>3</sub>	2.3	2.3	2.1	2.0	-
	CH <sub>2</sub> Si <sup>a</sup>	3.4	3.6	3.1	3.0	-
	CH <sub>2</sub> Si <sup>b</sup>	3.0	2.9	2.5	2.5	-
$^{13}\text{C}$	C-2	-	137.6	138.2	137.8	137.8
	C-4	-	123.1	124.1	125.5	129.5
	C-5	-	122.8	122.7	121.6	120.1
	NCH <sub>3</sub>	-	35.5	35.0	34.1	33.3
	CH <sub>3</sub> Si <sup>a</sup>	2.1	2.1	1.2	-0.29	-
	CH <sub>3</sub> Si <sup>b</sup>	7.0	4.0	2.6	2.1	-
	COCH <sub>3</sub>	17.8	17.9	17.9	17.5	-
	CO	174.0	173.5	173.6	173.5	-
	CH <sub>2</sub> Si <sup>a</sup>	45.7	42.8	42.3	41.5	-
	CH <sub>2</sub> Si <sup>b</sup>	42.9	42.3	41.1	40.6	-
$^{29}\text{Si}$	CH <sub>3</sub> Si <sup>a</sup>	26.9	27.5	25.4	18.4	-
	CH <sub>3</sub> Si <sup>b</sup>	-24.6	-51.1 (br)	-54.2	-54.4	-
Quantities used:						
(3.11)(mmol)		2	2	2	2	-
NMI (mmol)		-	1	2	4	2
Solvent : CDCl <sub>3</sub> , 2 ml						

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

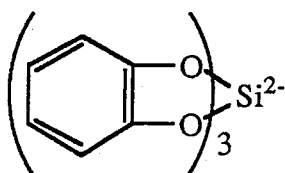
## **CHAPTER FOUR**

### ***Synthesis of Hexacoordinate Organosilylamides***

#### 4.1 INTRODUCTION :

Relative to carbon, silicon compounds with a coordination number less than four are usually not common. But the silicon atom is capable of increasing its coordination number to five or six or even seven, especially when it is bonded to an electronegative atom. Hexacoordinated silicon compounds can be neutral due to inter- and intramolecular interactions of the donor acceptor type, anionic or cationic complexes. Hexacoordinated silicon species have frequently been proposed as intermediates or transition state formed during the course of a chemical reaction<sup>7b,122,138,151,152</sup>. Such species are uncharged when they are formed by nucleophilic solvents such as hexamethylphosphoramide, dimethylformamide or dimethylsulphoxide, e.g., in the racemization<sup>151</sup>, hydrolysis or alcoholysis of chlorosilanes<sup>122</sup>. Anionic complexes result in the activation of SiH<sup>138</sup>, SiO<sup>138,153-156</sup>, SiN<sup>157</sup> and SiC<sup>92,142,158,159</sup> bonds by fluoride anions.

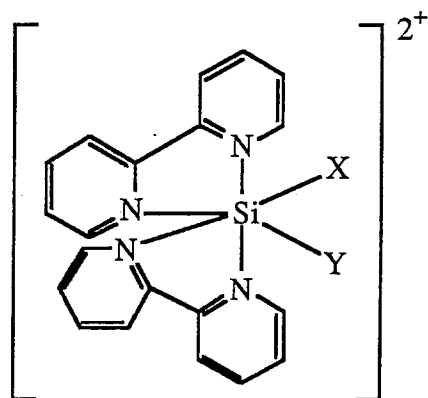
Hexafluorosilicate ion SiF<sub>6</sub><sup>2-</sup>, known<sup>160</sup> since the beginning of the 19th century, is the parent of the anionic complexes RSiF<sub>5</sub><sup>2-</sup>. The latter is obtained as a crystalline potassium salt by treating RSiCl<sub>3</sub> with excess of potassium fluoride in aqueous or aqueous/alcoholic solution<sup>161</sup>. Hexacoordinate anionic complexes with oxygen donors have been described only with chelating ligands. Most are salts of tris-chelate dianions which may be formed from both aromatic<sup>162</sup> and aliphatic<sup>163</sup> 1,2-diols. A typical example is spirocyclic anion Si(-OC<sub>6</sub>H<sub>4</sub>O)<sub>3</sub><sup>2-</sup> (4.1) which is



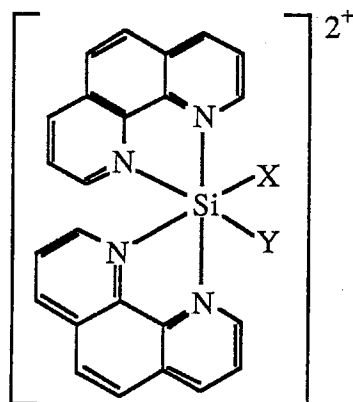
(4.1)

obtained from the reaction of catechol with silica<sup>164</sup>. X-ray study has shown<sup>49</sup> that each of the three cyclic ligands at the silicon is non planar, and the maximum distance from the plane is 0.037 Å. The anion assumes almost octahedral geometry. All OSiO angles differ from the ideal angles of 90° and 180° in the octahedron. The Si-O bonds are not equivalent (1.765-1.813 Å)<sup>49</sup>.

Many hexacoordinate complexes with neutral monodentate and bidentate nitrogen donors and some with oxygen donors are known<sup>152,165</sup>. A significant study of complexes formed with 2,2'-bipyridyl or 1,10-phenanthroline has resulted in the characterisation of bis-chelate dications of type (4.2)<sup>166</sup> and (4.3)<sup>167</sup> respectively.



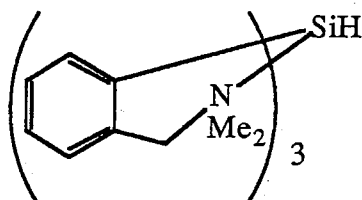
(4.2)



(4.3)

Groups X and Y range from hydroxyl, methoxyl and halogen to hydrogen, methyl and phenyl. Other silicon complexes of the type  $\text{Si}(\text{bipyridyl})_3\text{I}_4$ <sup>166</sup>,  $\text{Si}(\text{phenanthroline})_3\text{I}_4$ <sup>168</sup> and  $\text{Si}(\text{pyridine-N-oxide})_6\text{I}_4$ <sup>169</sup> have also been prepared

in which silicon cation of charge +4 are present. Recently, preliminary structural data have been prepared for O-silyl-substituted N,N-dimethylaminomethylbenzene (4.4) with a suggested heptacoordinate silicon atom<sup>170</sup>.



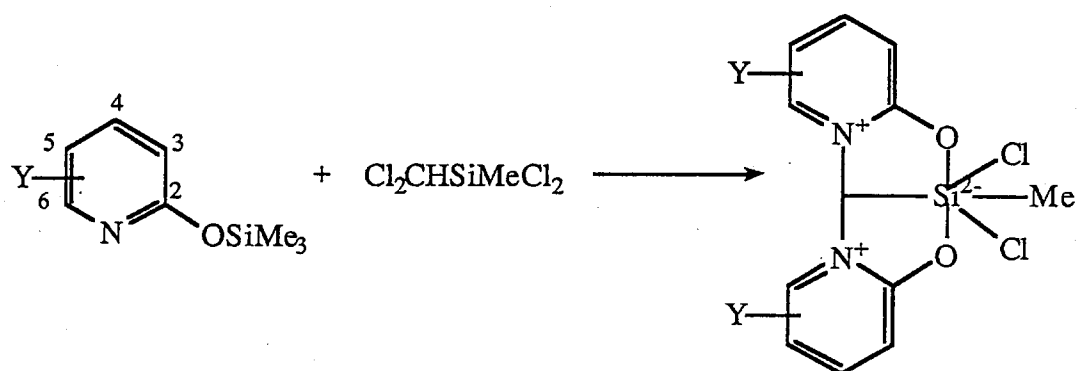
(4.4)

In the course of our studies on the mapping of nucleophilic substitution in solution and the reactivity of hypervalent silicon species, we were interested in exploring the conditions under which hexacoordinated silicon compounds may be formed.

Following the concepts developed by Dunitz<sup>66</sup>, who demonstrated that the interactions between nucleophilic and electrophilic centres in the crystal are a good picture of transition state or intermediates of corresponding chemical reactions. We were interested in synthesising new hexacoordinated silicon compounds and to study their crystal structures although in this latter aspect we were unsuccessful.

## 4.2 RESULTS AND DISCUSSION :

The reaction of 2 equivalents of 2-trimethylsiloxy-6-methylpyridine (4.5a) with 1 equivalent of dichloromethyl(methyldichloro)silane furnished a compound, m.p. 178°C. The mass spectrum gave the molecular ion peak at  $m/z$  342/344/346 (10:6:1) indicating the presence of two chlorines in it. In the silicon-29 NMR



- (4.5) a) Y=6-Me  
 b) Y=H  
 c) Y=3-OMe

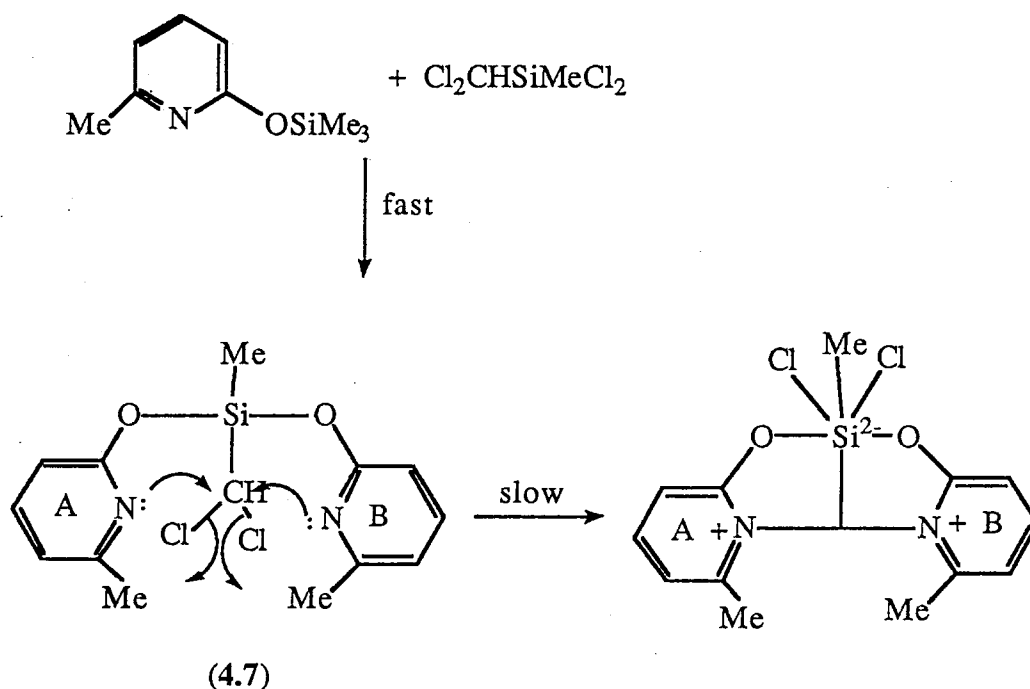
- (4.6) a) Y=6-Me  
 b) Y=H  
 c) Y=3-OMe

spectrum the peak at -120.4 ppm was assigned for the hexacoordinated silicon. In the proton NMR spectrum the singlet at 5.3 ppm was assigned to the methine proton. Therefore, structure (4.6a) was assigned to the reaction product. Only one set of carbon-13 signals were observed for (4.6a) for both the aromatic rings which showed that the two rings were in identical environments.

Similarly, the reactions of 2-trimethylsiloxy-6-methylpyridine (4.5b) and 2-trimethylsiloxy-3-methoxypyridine (4.5c) with dichloromethyl(methyldichloro)silane furnished the corresponding hexacoordinated silicon compounds (4.6b) and (4.6c) respectively.

We observed that the reaction proceeds through the intermediate (4.7) and then finally rearranged to give the hexacoordinated species. Formation of the intermediate 4.7 was a fast process and the 2nd step i.e., the formation of the hexacoordinated species was a slow process. For example when the NMR of a mixture of 2-trimethylsiloxy-6-methylpyridine (4.5a) and dichloromethyl(methyldichloro)silane was recorded after 2 hrs., we observed a peak at -23.2 ppm in silicon-29 NMR which suggested that the silicon atom was in tetravalent state. There was only one set of peaks in carbon-13 NMR. The values were 108.9, 117.3,

139.7, 156.3, 160.0 ppm. which showed that both the rings A and B were in pyridine form as shown in Scheme 4.1. An additional peak at -120.4 ppm in silicon-29 NMR was observed when the NMR of the reaction mixture was recorded after 10 hrs, which showed the formation of the hexacoordinated species. Two sets of signals were observed in the carbon-13 NMR. The signals at 108.6, 118.1, 140.3, 156.4, and 159.4 ppm was assigned for the rings, which were in pyridine form and the signals at 113.8, 115.3, 144.6, 149.8, 165.8 ppm was assigned for the rings, which were in pyridinium ion form. The peak at -23.2 ppm that was observed in silicon-29 NMR and the carbon-13 chemical shifts observed, when the NMR of the reaction mixture was recorded after 2 hrs, disappeared completely after 45 hrs and a single peak at -120.4 ppm in silicon-29 NMR and a single set of resonance in carbon-13 NMR were observed, which confirmed the complete conversion to six coordinated silicon species to give the compound (4.6a) as shown in Scheme 4.1.



Scheme 4.1

The extent of O-Si bond formation of **4.6a** was determined by comparing their carbon-13 chemical shifts with 6-Me substituted pyridone derivatives (Figure 4.1) and was found to be approximately 60%. Comparison of carbon-13 chemical shifts of **4.6b** and **4.6c** with their respective pyridone derivatives (Figures 4.2 and 4.3) showed that they were approximately 50% and 70% respectively.

The stereochemistry of the hexacoordinated silicon compounds were found to be solvent dependent. For example, when the silicon-29 NMR of the compound (**4.6b**) was recorded in CD<sub>3</sub>OD, only one signal at -127.0 ppm was observed. There was only one set of signals in carbon-13 NMR. But when the silicon-29 NMR was recorded in DMSO-d<sub>6</sub>, an additional peak at -131.1 ppm was observed and an additional set of signals, which were very close together was observed in carbon-13 NMR. Two sets of peaks each for -CH carbon (62.6, 65.3 ppm) and SiMe (5.5, 13.0 ppm) were observed in carbon-13 NMR, which showed that the compound (**4.6b**) can exist in two different isomers in DMSO-d<sub>6</sub>. Similarly, we observed two signals in silicon-29 NMR for **4.6c**.

Model study has shown that there could be two possible major isomers as shown in Figures 4.4 and 4.5. One isomer may be due to two chlorine and oxygen atoms trans to each other with the methyl group in the axial position. Here the two aromatic rings are flanked by about 130° as shown in Figure 4.4. The other isomer may be due to the two chlorine and oxygen atoms cis to each other with the methyl group in the axial position. The aromatic rings are flanked by about 180° as shown in Figure 4.5.

Reaction of **4.5a** with antimony trifluoride in benzene furnished a compound, m.p.153°C. The mass spectrum gave the molecular ion peak at 310. A triplet at



Figure 4.1 Comparison of C-13 chemical shifts of 4.6a with  
6-Me silylpyridones (2.1B, Y=6-Me)

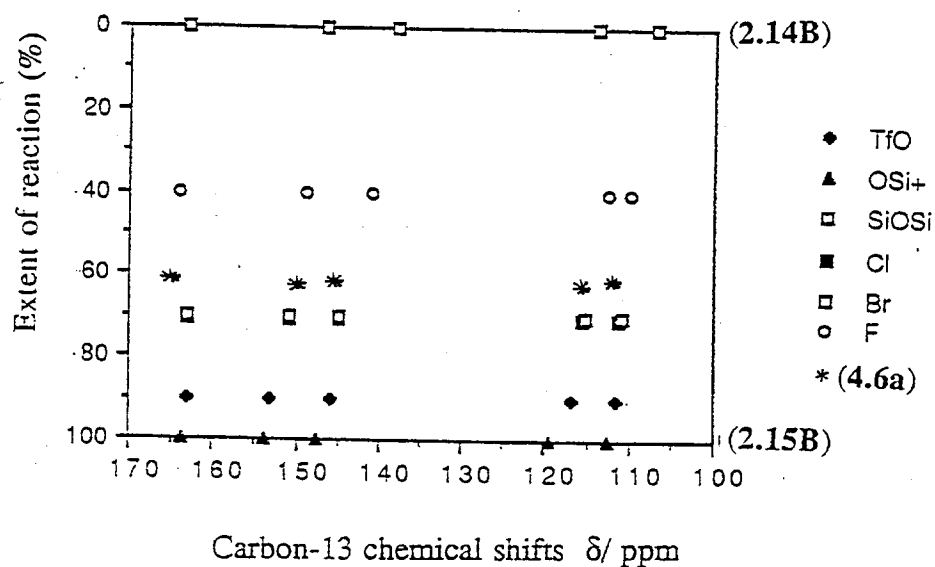


Figure 4.2 Comparison of C-13 chemical shifts of 4.6b with  
unsubstituted silylpyridones (2.1B, Y=H)

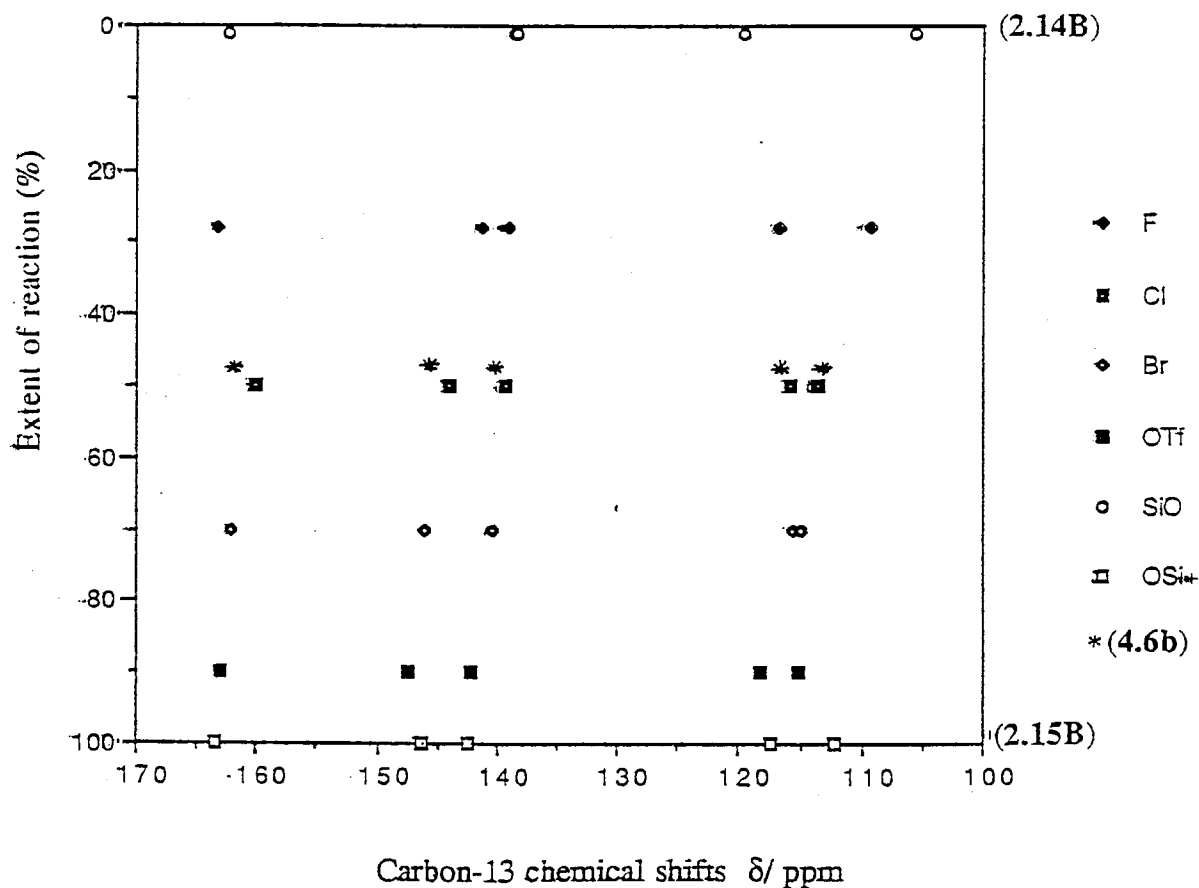
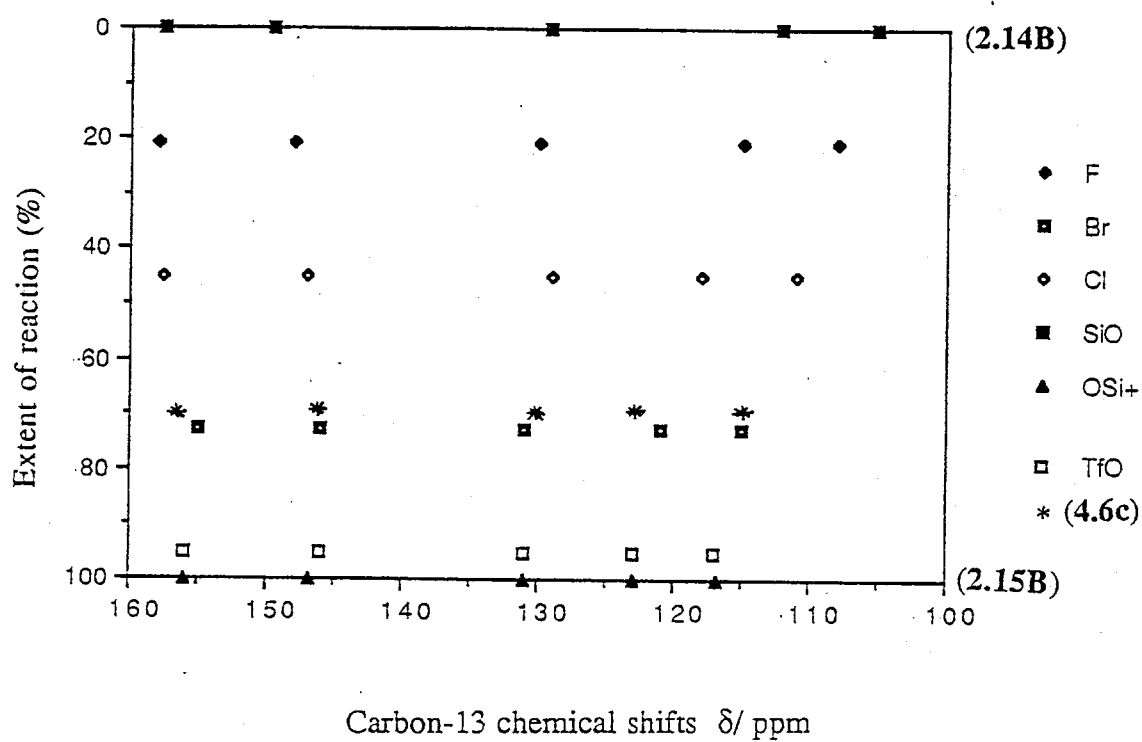


Figure 4.3 Comparison of C-13 chemical shifts of 4.6c, with  
3-OMe silylpyridones (2.1B, Y=3-OMe)



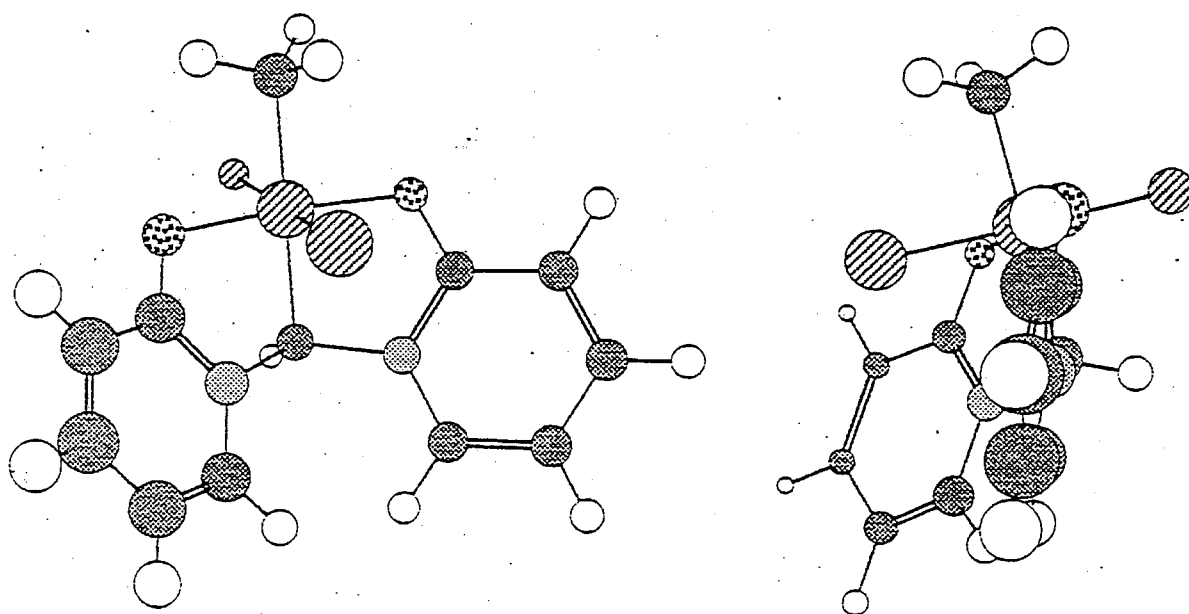


Figure 4.4 A possible isomer of 4.6b

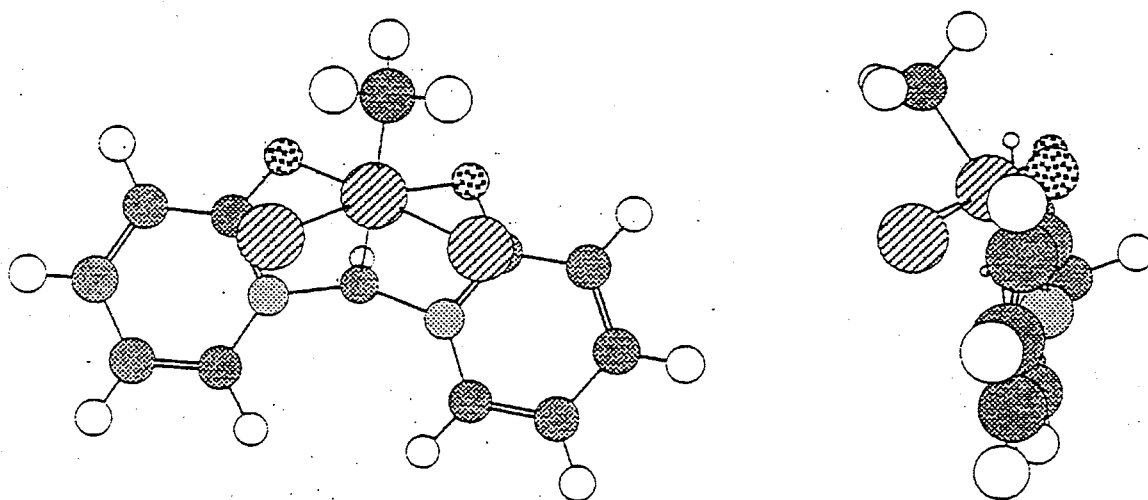
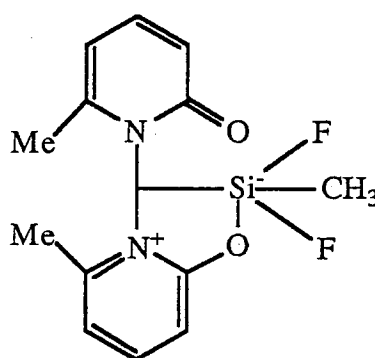


Figure 4.5 An alternative isomer of 4.6b

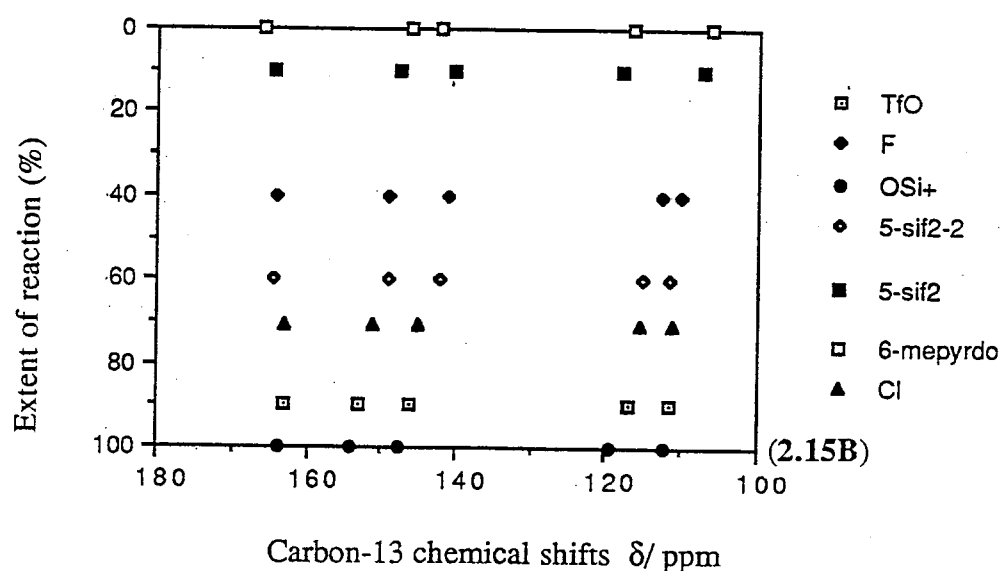
-82.9 ppm with coupling constant 262.7 Hz observed in silicon-29 NMR was assigned to the pentavalent silicon. Although this a rather high value for pentacoordinate silicon it is observed that fluorine has a high field shielding effect compared with chlorine. The silicon-29 chemical shift of difluoromethylsilylpyrid-2-one (**2.10B**, Y=H) is -59.9 ppm which shows that there is probably some additional coordination from the pyridone ring. A singlet at 6.0 ppm in proton NMR was assigned to the methine proton. Two signals in the carbon-13 NMR each at 20.6 and 21.4 ppm were observed for the methyl group attached to the aromatic rings.



(4.8)

We also observed two sets of signals in carbon-13 NMR for the ring, which showed that the two aromatic rings were in two different forms. Close examinations have shown that one set of signals were very similar to that of disiloxane (**2.14B**, Y=6-Me, Chapter-2B, Table 2.6B), where the ring was in pyridone form and the other set to disiloxane triflate (**2.15B**, Y=6-Me, Chapter-2B, Table 2.6B) where the ring was in pyridinium ion form. Therefore, the structure **4.8** was assigned to the reaction product. The extent of reaction for one oxygen atom was about 10% and about 60% for the other oxygen and the results are shown in Figure 4.6

Figure 4.6 Comparison of C-13 chemical shifts of difluoromethylsilylmethyl-bis(6-methylpyrid-2-one) (4.8) with 6-Me silyl pyridones.



Several attempts to recrystallise the reaction product either by using different solvent mixtures or by sublimation were made but failed. So, we were unable to determine the X-ray structure of our hexacoordinated complexes.

## ***EXPERIMENTAL***

## PURIFICATION OF STARTING REAGENTS

Chemicals were purified either by distillation, or by simply storing over molecular sieves under nitrogen prior to use. Distillations were carried out at reduced pressure where appropriate. The pressure was adjusted to achieve a distillation temperature of between 50-100°C if possible.

Chloroform: BDH Chemicals Ltd., 'Analar', was washed several times with water to remove the ethanol stabilizer, dried with potassium carbonate and distilled in the dark from calcium chloride, and finally stored under nitrogen in a light proof container, over 4A molecular sieve.

Hexane: BDH Chemicals Ltd., 'Analar'. Distilled from sodium wire.

Hexamethylphosphoramide: Aldrich Chemical Co. Ltd., distilled from phosphorus pentoxide and stored over 4A molecular sieve.

Tetrahydrofuran: Rathburn Chemicals Ltd., HPLC grade; refluxed and distilled from calcium hydride under nitrogen.

Ether: BDH Chemicals Ltd., dried with sodium wire, followed by refluxing and distilling from calcium hydride under nitrogen.

Benzene: BHD Chemicals Ltd., 'Analar', dried with calcium chloride prior to distillation.

a) The following compounds were allowed to stand for at least two days over 4A molecular sieve, distilled and stored over 4A molecular sieve under nitrogen.

1-Methylimidazole (Aldrich Chemical Co. Ltd.)

1-Methyl-2-pyridone (Aldrich Chemical Co. Ltd.)

b) Reagent grade solvents and the chemicals listed below were stored over 4A molecular sieve and used without further purification:

Dichloromethane-d<sub>2</sub> (Aldrich Chemical Co. Ltd., GOLD LABEL,  
99.6 atom % D)

Acetonitrile-d<sub>3</sub> (Aldrich Chemical Co. Ltd., GOLD LABEL, 99 atom % D)

Acetone-d<sub>6</sub> (Aldrich Chemical Co. Ltd., GOLD LABEL, 99.5 atom % D)

Chloroform-d<sub>1</sub> (Aldrich Chemical Co. Ltd., GOLD LABEL, 99.8 atom % D)

Methanol-d<sub>4</sub> (Aldrich Chemical Co. Ltd. GOLD LABEL. 99.8 atom % D)

c) The following compounds were distilled from potassium hydroxide and 4A molecular sieve:

Pyridine (Aldrich Chemical Co. Ltd.)

Triethylamine (Aldrich Chemical Co. Ltd.)

d) Since some of the chemicals are very reactive towards molecular sieves, distillations were carried out in the absence of any drying agents in these cases:

Trifluoromethanesulphonic acid (Aldrich Chemicals Co. Ltd.)

Trimethylsilyl triflate (Aldrich Chemicals Co. Ltd.)

Bis(trimethylsilyl)acetamide (Aldrich Chemical Co. Ltd.)

N-Methyl-N-trimethylsilylacetamide (Fluka AG, purum)

e) The following reagents have been used without any purification:

Chloromethyldimethylchlorosilane (Aldrich Chemical Co. Ltd.)

Chloromethyldichloromethylsilane (Aldrich Chemical Co. Ltd.)

Chloromethyltrichlorosilane (Aldrich Chemical Co. Ltd.)

Dichloromethyl(methyldichloro)silane (Fluorochem. Ltd.)

Antimony trifluoride (Aldrich Chemical Co. Ltd.)

N,N-diethyltrimethylsilylamine (Aldrich Chemical Co. Ltd.)



2-Hydroxypyridine (Aldrich Chemical Co. Ltd.)

3-Methoxy-2(1H)-pyridone (Aldrich Chemicals Co. Ltd.)

2-Hydroxy-3-nitropyridine (Aldrich Chemical Co. Ltd.)

2-Hydroxy-6-methylpyridine (Aldrich Chemical Co. Ltd.)

5-Chloro-2-pyridinol (Aldrich Chemical Co. Ltd.)

6-Chloro-2-pyridinol (Aldrich Chemical Co. Ltd.)

### **NMR PARAMETERS**

All spectral measurements were made on a Jeol FX90 Q n.m.r. spectrometer, equipped with a tunable, multinuclear probe. Tetramethylsilane was taken as the reference. The spectral parameters were generally as follows:

$^1\text{H}$ : spectral width, 89.56 MHz, 1000 Hz; pulse width, 20 $\mu\text{s}$ ; pulse delay, 0.1s.

$^{13}\text{C}$ : spectral width, 22.5 MHz, 5302 Hz (-16 to 219 ppm); pulse width, 12 $\mu\text{s}$ ; pulse delay, 1.0s; completely decoupled, exponential window, 1.24 Hz

$^{29}\text{Si}$ : spectral width, 17.76 MHz, 4000 Hz (65 to -160 ppm); pulse width, 12 $\mu\text{s}$ ; pulse delay, 15s; proton decoupled, exponential window, 18 Hz.

### **SOURCES OF ERROR**

Extensive precautions were taken to exclude moisture, when handling moisture sensitive compounds, but the possibility of a small percentage of hydrolysis cannot be entirely discounted.

All compounds including both silanes and nucleophiles were handled under nitrogen. The normal techniques used for handling moisture sensitive compounds were employed i.e. transfer in dry nitrogen glove box or via stainless steel needles etc.. Chemicals were stored in reagent bottles with either PTFE-silicon rubber septa valves(Pierce Miniert Valves) or PTFE-silicon rubber septa caps. The septa were replaced regularly because they reacted with reactive silanes e.g., triflic acid, trimethylsilyltriflate and also to prevent moisture entering through the punctures. In addition, reagent bottles were stored in a silica gel dessicator or used entirely in a nitrogen glove box. Fine gauge stainless steel needles with a non-coring tip were used to minimise the damage to septa.

Weighings were done on a Sartorius 2000 MP digital balance. Hamilton gas tight syringes of appropriate size were used for measuring quantities of reagents.

Accuracy of these syringes were determined by weighing measured volumes of distilled water. The maximum deviation from the indicated volume was found to be  $\pm 0.7\%$ .

### **MELTING POINTS:**

These were determined on a Electrothermal Digital melting point apparatus.

### **ELEMENTAL ANALYSIS:**

Elemental analysis were carried out by MEDAC LTD. The elemental analysis was difficult with some of our new compounds. Several samples of some compounds were analysed and found to be acceptable by H, N (and halogen) but C

was frequently low. This may be due to carbide formation.

### **MASS SPECTRA**

Mass spectra were recorded on a VG20-250 mass spectrometer.

**GENERAL PROCEDURE FOR THE SILYLATION OF 2-PYRIDONE  
WITH DIETHYLAMINETRIMETHYLSILANE<sup>171</sup>**

25 mmol of 2- Pyridone was dissolved in 10 ml benzene. 25 mmol of diethylamine-trimethylsilane was added to it and the reaction mixture was refluxed for 5 hrs. under nitrogen. The volatile materials were removed under reduced pressure and finally the product was isolated by distillation.

The siloxypyridines used for the synthesis of silylpyridones used as an intermediates without analysis other than NMR.

i) 2-Trimethylsiloxypyridine (2.2B, Y=H)

2- Pyridone 2.38 g

Diethylaminetrimethylsilane 4.74 ml

Yield 3.02 g, 72.3%

B.P. 37°C / 1 mm Hg (Lit<sup>171</sup>. 34-38°C / 1 mm Hg)

NMR             $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H     0.35 (s, 9H, SiMe<sub>3</sub>), 6.6-8.1 (m, 4H, arom)

<sup>13</sup>C    0.52, 112.3, 116.2, 138.3, 146.7, 162.2

<sup>29</sup>Si    19.9

ii) 2-Trimethylsiloxy-6-methylpyridine (2.2B, Y=6-Me)

2-Hydroxy-6-methylpyridine 2.73 g

Diethylaminetrimethylsilane 4.74 ml

Yield 2.94 g, 65%

B.P. 45°C / 0.2 mm Hg (Lit<sup>171</sup>. 44°C / 0.2 mm Hg)

NMR             $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H      0.34 (s, 9H, SiMe<sub>3</sub>), 2.33 (s, 3H, Me),  
           6.4-7.4 (m, 3H, arom)

<sup>13</sup>C      0.57, 24.0, 109.2, 115.6, 139.0, 156.2, 162.2,

<sup>29</sup>Si    19.3

iii) 2-Trimethylsiloxy-3-methoxypyridine (2.2B, Y=3-OMe)

3-Methoxy-2-hydroxypyridine 3.13 g

Diethylaminetrimethylsilane 4.74 ml

Yield 3.94 g, 80%

B.P. 66°C / 0.5 mm Hg

NMR             $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H      0.36 (s, 9H, SiMe<sub>3</sub>), 3.75 (s, 3H, OMe),  
           6.8-7.7 (m, 3H, arom)

<sup>13</sup>C      -0.57, 55.0, 116.6, 117.8, 137.0, 114.4, 152.5

<sup>29</sup>Si    20.7

iv) 2-trimethylsiloxy-5-chloropyridine (2.2B, Y=5-Cl)

5-Chloro-2-hydroxypyridine 3.24 g

Diethylaminetrimethylsilane 4.74 ml

Yield 4.24 g, 84.4%

B.P. 60°C / 2 mm Hg

NMR             $\delta$ / ppm (CD<sub>3</sub>CN, TMS)

<sup>1</sup>H      0.34 (s, 9H, SiMe<sub>3</sub>), 6.5-8.1 (m, 3H, arom)

$^{13}\text{C}$  -0.23, 110.6, 116.2, 140.7, 147.9, 161.8,

$^{29}\text{Si}$  21.4

v) 2-Trimethylsiloxy-3-nitropyridine (2.2B, Y=3-NO<sub>2</sub>)

2-Hydroxy-3-nitropyridine 3.5 g

Diethylaminetrimethylsilane 4.74 ml

Yield 4.19 g, 79%

B.P. 92°C / 0.5 mm Hg

NMR  $\delta$ / ppm (CD<sub>3</sub>CN+CDCl<sub>3</sub>, 1:1, TMS)

$^1\text{H}$  0.40 (s, 9H, SiMe<sub>3</sub>), 7.0-8.3 (m, 3H, arom)

$^{13}\text{C}$  -0.34, 116.9, 134.8, 142.5, 151.6, 154.7

$^{29}\text{Si}$  25.5

vi) 2-Trimethylsiloxy-6-chloropyridine (2.2B, Y=6-Cl)

6-Chloro-2-hydroxypyridine 3.24 g

Diethylaminetrimethylsilane 4.74 ml

Yield 4.27 g, 85%

B.P. 67°C / 3 mm Hg

NMR  $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

$^1\text{H}$  0.36 (s, 9H, SiMe<sub>3</sub>), 6.5-7.6 (m, 3H, arom)

$^{13}\text{C}$  -0.29, 113.5, 123.8, 138.4, 145.3, 160.8

$^{29}\text{Si}$  22.4

**GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE  
SILYL CHLORIDES FROM SILYLATED PYRIDONES AND  
CHLOROMETHYLDIMETHYLCHLOROSILANE**

Chloromethyldimethylchlorosilane in dry ether was added slowly into a stirred solution of 2-trimethylsiloxy pyridine (both are equimolar amounts) in dry ether under nitrogen. The reaction mixture was stirred for 1h. The solid was filtered under nitrogen and dried under vacuum.

i) Synthesis of chlorodimethylsilylmethylpyrid-2-one (2.4Ba, Y=H)

2-Trimethylsiloxy pyridine 0.41g, 2.46 mmol

Chloromethyldimethylchlorosilane 325  $\mu$ l, 2.46 mmol

Yield 0.43 g, 87%

M.P. 91-94°C

NMR

$\delta$ / ppm ( $\text{CDCl}_3 + \text{CD}_3\text{CN}$ , 1:1, TMS)

$^1\text{H}$  0.64 (s, 6H,  $\text{SiMe}_2$ ), 3.7 (s, 2H,  $\text{NCH}_2$ ),  
6.8-7.9 (m, 4H, arom)

$^{13}\text{C}$  7.5, 42.2, 113.6, 115.8, 140.0, 143.3, 160.1

$^{29}\text{Si}$  -41.1

Analysis

Found: C, 46.79; H, 6.06; N, 6.78; Cl, 17.14.

$\text{C}_8\text{H}_{12}\text{NOCISi}$  calcd.: C, 47.63; H, 6.01; N, 6.94;

Cl, 17.57.

ii) Synthesis of chlorodimethylsilylmethyl-6-methylpyrid-2-one (2.4Ba, Y= 6-Me)

2-Trimethylsiloxy-6-methylpyridine 0.4 g, 2.21 mmol

Chloromethyldimethylchlorosilane 293  $\mu$ l, 2.21 mmol

Yield 0.40 g, 84%

M.P. 99-104°C

NMR

$\delta$ / ppm (CDCl<sub>3</sub>+2 drops CD<sub>3</sub>OD, TMS)

<sup>1</sup>H 0.53 (s, 6H, SiMe<sub>2</sub>), 2.7 (s, 3H, Me)  
3.7 (s, 2H, NCH<sub>2</sub>), 6.8-8.0 (m, 3H, arom)

<sup>13</sup>C 1.21, 20.6, 37.8, 111.3, 115.6, 144.8,  
151.0, 163.4

<sup>29</sup>Si -24.7

Analysis

Found: C, 49.90; H, 6.46; N, 6.42; Cl, 16.50.

C<sub>9</sub>H<sub>14</sub>NOCISi calcd.: C, 50.10; H, 6.54; N, 6.49;

Cl, 16.43.

iii) Synthesis of chlorodimethylsilylmethyl-3-methoxypyrid-2-one  
(2.4Ba, Y= 3-OMe)

2-Trimethylsiloxy-3-methoxypyridine 0.30 g, 1.52 mmol

Chloromethyldimethylchlorosilane 202  $\mu$ l, 1.52 mmol

Yield 0.31 g, 88.1%

M.P. 96-99°C



<u>NMR</u>	$\delta$ / ppm (CD <sub>3</sub> CN, TMS)
<sup>1</sup> H	0.62 (s, 6H, SiMe <sub>2</sub> ), 3.7 (s, 2H, NCH <sub>2</sub> ), 3.9 (s, 3H, OMe), 6.7-7.6 (m, 3H, arom)
<sup>13</sup> C	6.4, 43.6, 56.6, 110.9, 118.0, 129.5, 147.2, 157.6
<sup>29</sup> Si	-32.0
<u>Mass</u>	m/z: 231/233 (3:1, M <sup>+</sup> ), 216/218 (3:1), 200/202 (3:1), 196, 181.
<u>Analysis</u>	Found: C, 44.24; H, 6.01; N, 5.65. C <sub>9</sub> H <sub>14</sub> NO <sub>2</sub> ClSi calcd.: C, 46.64; H, 6.09; N, 6.04.

iv) Synthesis of chlorodimethylsilylmethyl-5-chloropyrid-2-one (2.4Ba, Y=5-Cl)

2-Trimethylsiloxy-5-chloropyridine 0.54 g, 2.69 mmol

Chloromethyldimethylchlorosilane 356  $\mu$ l, 2.69 mmol

Yield 0.56 g, 88.2%

M.P. 99-106°C

<u>NMR</u>	$\delta$ / ppm (CD <sub>3</sub> OD, TMS)
<sup>1</sup> H	0.46 (s, 6H, SiMe <sub>2</sub> ), 4.0 (s, 2H, NCH <sub>2</sub> ), 7.2-8.4 (m, 3H, arom)
<sup>13</sup> C	1.2, 43.0, 116.2, 120.8, 138.2, 144.7, 160.9.
<sup>29</sup> Si	-17.1
<u>Mass</u>	m/z: 235/237/239 (10:6:1, M <sup>+</sup> ), 220/222/224 (10:6:1) 200/202 (3:1), 165.
<u>Analysis</u>	Found: C, 40.54; H, 4.72; N, 5.92. C <sub>8</sub> H <sub>11</sub> NOCl <sub>2</sub> Si calcd.: C, 40.69; H, 4.69; N, 5.93.

v) Synthesis of chlorodimethylsilylmethyl-3-nitropyrid-2-one (2.4Ba, Y= 3-NO<sub>2</sub>)

2-Trimethylsiloxy-3-nitropyridine 0.57 g, 2.69 mmol

Chloromethyldimethylchlorosilane 356  $\mu$ l, 2.69 mmol

Yield 0.51 g, 77%

M.P. 96-100°C

NMR $\delta$ / ppm (CD<sub>3</sub>CN+2 drops DMSO-d<sub>6</sub>, TMS)<sup>1</sup>H 0.50 (s, 6H, SiMe<sub>2</sub>), 3.7 (s, 2H, NCH<sub>2</sub>),

6.7-8.4 (m, 3H, arom)

<sup>13</sup>C -0.57, 43.8, 105.9, 136.7, 140.1, 146.4, 156.6.<sup>29</sup>Si -25.0Massm/z : 246/248 (3:1, M<sup>+</sup>), 231/233 (3:1), 211, 185/187  
(3:1), 165.AnalysisFound: C, 39.21; H, 4.52; N, 11.39. C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub>ClSi  
calcd.: C, 38.95; H, 4.49; N, 11.35vi) Synthesis of chlorodimethylsilylmethyl-6-chloropyrid-2-one (2.4Ba, Y= 6-Cl)

2-Trimethylsiloxy-6-chloropyridine 0.47 g, 2.34 mmol

Chloromethyldimethylchlorosilane 310  $\mu$ l, 2.34 mmol

Yield 0.47 g, 85%

M.P. 99-101°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.67 (s, 6H, SiMe<sub>2</sub>), 3.7 (s, 2H, NCH<sub>2</sub>),

6.8-7.8 (m, 3H, arom)

<sup>13</sup>C 7.3, 42.3, 112.5, 113.1, 140.5, 143.0, 164.2.

	$^{29}\text{Si}$ -40.9
<u>Mass</u>	m/z: 235/237/239 (10:6:1, $\text{M}^+$ ), 220/222/224 (10:6:1), 202/204 (3:1), 165.
<u>Analysis</u>	Found: C, 40.80; H, 4.63; N, 6.27. $\text{C}_8\text{H}_{11}\text{NOCl}_2\text{Si}$ calcd.: C, 40.69; H, 4.69; N, 5.93.

**GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE  
SILYL BROMIDES FROM SILYLATED PYRIDONES AND  
BROMOMETHYLDIMETHYLCHLOROSILANE**

The synthesis was the same as for the synthesis of five coordinate silyl chlorides. Chloromethyldimethylchlorosilane was replaced by bromomethyldimethylchlorosilane.

i) Bromodimethylsilylmethylpyrid-2-one (2.5B, Y= H)

2-Trimethylsiloxypyridine 0.35 g, 2.09 mmol

Bromomethyldimethylchlorosilane 286  $\mu\text{l}$ , 2.09 mmol

Yield 0.44 g, 85.6%

M.P. 102-104°C

<u>NMR</u>	$\delta$ / ppm ( $\text{CD}_3\text{CN}+\text{CDCl}_3$ , 1:1, TMS)
	$^1\text{H}$ 0.72 (s, 6H, $\text{SiMe}_2$ ), 3.9 (s, 2H, $\text{NCH}_2$ ), 6.9-8.1 (m, 4H, arom)
	$^{13}\text{C}$ 1.9, 44.8, 115.0, 115.7, 141.0, 146.1, 163.1.
	$^{29}\text{Si}$ -18.4

<u>Mass</u>	m/z: 166 (M <sup>+</sup> -Br), 136, 106, 78.
<u>Analysis</u>	Found: C, 37.95; H, 4.76; N, 5.51. C <sub>8</sub> H <sub>12</sub> NOBrSi calcd.: C, 39.01; H, 4.92; N, 5.69.

ii) Bromodimethylsilylmethyl-6-methylpyrid-2-one (2.5B, Y= 6-Me)

2-Trimethylsiloxy-6-methylpyridine 0.43 g, 2.38 mmol

Bromomethyldimethylchlorosilane 324μl, 2.38 mmol

Yield 0.54 g, 87%

M.P. 108-111°C

<u>NMR</u>	δ/ ppm (CDCl <sub>3</sub> +2 drops CD <sub>3</sub> OD, TMS)
<sup>1</sup> H	0.45 (s, 6H, SiMe <sub>2</sub> ), 2.7 (s, 3H, Me), 3.7 (s, 2H, NCH <sub>2</sub> ), 6.8-8.0 (m, 3H, arom)
<sup>13</sup> C	1.7, 20.7, 37.9, 111.5, 115.2, 144.8, 151.6, 163.7
<sup>29</sup> Si	-21.3

<u>Analysis</u>	Found: C, 41.67; H, 5.37; N, 5.40. C <sub>9</sub> H <sub>14</sub> NOBrSi calcd.: C, 41.54; H, 5.42; N, 5.38.
-----------------	---

iii) Bromodimethylsilylmethyl-3-methoxypyrid-2-one (2.5B, Y= 3-OMe)

2-Trimethylsiloxy-3-methoxypyridine 0.36 g, 1.83 mmol

Bromomethyldimethylchlorosilane 250μl, 1.83 mmol

Yield 0.45 g, 90%

M.P. 105-108°C

NMR $\delta$ / ppm ( $\text{CDCl}_3$ +2 drops  $\text{CD}_3\text{OD}$ , TMS) $^1\text{H}$  0.73 (s, 6H,  $\text{SiMe}_2$ ), 4.0 (s, 3H, OMe), 4.2 (s, 2H,  $\text{NCH}_2$ ), 7.1-7.9 (m, 3H, arom) $^{13}\text{C}$  -0.63, 44.9, 58.0, 116.1, 122.1, 132.1, 147.3, 154.9. $^{29}\text{Si}$  -14.3AnalysisFound: C, 36.85; H, 5.57; N, 4.87.  $\text{C}_9\text{H}_{14}\text{NO}_2\text{BrSi}$ 

calcd.: C, 39.14; H, 5.11; N, 5.07.

iv) Bromodimethylsilylmethyl-5-chloropyrid-2-one (2.5B, Y=5-Cl)

2-Trimethylsiloxy-5-chloropyridine 0.53 g, 2.64 mmol

Bromomethyldimethylchlorosilane 360  $\mu\text{l}$ , 2.64 mmol

Yield 0.65 g, 88%

M.P. 107-112°C

NMR $\delta$ / ppm ( $\text{CDCl}_3$ +2 drops  $\text{CD}_3\text{OD}$ , TMS) $^1\text{H}$  0.44 (s, 6H,  $\text{SiMe}_2$ ), 4.4 (s, 2H,  $\text{NCH}_2$ ), 7.4-8.6 (m, 3H, arom) $^{13}\text{C}$  -0.34, 42.9, 115.8, 122.0, 138.9, 145.4, 160.3. $^{29}\text{Si}$  -12.7Mass $m/z$ : 279/281/283 (3:4:1,  $\text{M}^+$ ), 264/266/268 (3:4:1), 200/202 (3:1), 186/188 (3:1)AnalysisFound: C, 34.00; H, 4.09; N, 4.99.  $\text{C}_8\text{H}_{11}\text{NOClBrSi}$ 

calcd.: C, 34.24; H, 3.95; N, 4.99

v) Bromodimethylsilylmethyl-3-nitropyrid-2-one (2.5B, Y=3-NO<sub>2</sub>)

2-Trimethylsiloxy-3-nitropyridine 0.56 g, 2.64 mmol

Bromomethyldimethylchlorosilane 360  $\mu$ l, 2.64 mmol

Yield 0.69 g, 90%

M.P. 110-112°C

NMR $\delta$ / ppm (CD<sub>3</sub>CN; TMS)<sup>1</sup>H 0.76 (s, 6H, SiMe<sub>2</sub>), 3.9 (s, 2H, NCH<sub>2</sub>),

7.1-8.7 (m, 3H, arom)

<sup>13</sup>C 1.5, 45.0, 111.2, 135.7, 141.4, 146.5, 157.8<sup>29</sup>Si -27.9Massm/z: 292/290 (1:1, M<sup>+</sup>), 211, 181.AnalysisFound: C, 34.88; H, 3.93; N, 10.09. C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub>BrSi

calcd.: C, 33.00; H, 3.81; N, 9.62

vi) Bromodimethylsilylmethyl-6-chloropyrid-2-one (2.5B, Y= 6-Cl)

2-Trimethylsiloxy-6-chloropyridine 0.49 g, 2.44 mmol

Bromomethyldimethylchlorosilane 333  $\mu$ l, 2.44 mmol

Yield 0.60 g, 87.7%

M.P. 105-109°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>+2 drops CD<sub>3</sub>OD, TMS)<sup>1</sup>H 0.55 (s, 6H, SiMe<sub>2</sub>), 3.9 (s, 2H, NCH<sub>2</sub>),

6.8-8.1 (m, 3H, arom)

<sup>13</sup>C 1.7, 40.1, 113.0, 114.7, 141.3, 144.7, 163.8

$^{29}\text{Si}$  -27.4Massm/z: 279/281/283 (3:4:1,  $\text{M}^+$ ), 264/266/268 (3:4:1),  
200/202 (3:1), 186/188 (3:1)AnalysisFound: C, 33.58; H, 4.22; N, 4.99.  $\text{C}_8\text{H}_{11}\text{NOCIBrSi}$   
calcd.: C, 34.24; H, 3.95; N, 4.99

**GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE  
SILYL FLUORIDES FROM FIVE COORDINATE SILYL CHLORIDES  
AND ANTIMONY TRIFLUORIDE**

5 mmol of pentacoordinated silyl chloride was dissolved (or suspended) in 5 ml dry benzene under nitrogen. 1.7 mmol of antimony trifluoride ( $\text{SbF}_3$ ) was added to it and the reaction mixture was stirred for 0.5 hr.. The reaction mixture was then diluted with excess water and extracted with chloroform (3 x 75 ml). The washed extract was dried over anhydrous magnesium sulphate and distilled under the rotary evaporator to obtain a colourless crystalline solid which was finally dried under vacuum.

i) Fluorodimethylsilylmethylpyrid-2-one (2.7B, Y=H)

Chlorodimethylsilylmethylpyrid-2-one 1.0 g

 $\text{SbF}_3$  0.30 g

Yield 0.57 g, 92%

M.P. 82-86°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.32 (d, <sup>3</sup>J<sub>HSiF</sub> = 6.8 Hz, 6H, SiMe<sub>2</sub>), 3.2 (s, 2H, NCH<sub>2</sub>), 6.5-7.7 (m, 4H, arom)<sup>13</sup>C 1.8 (d, <sup>2</sup>J<sub>CSiF</sub> = 25 Hz, SiMe), 39.5 (d, <sup>2</sup>J<sub>CSiF</sub> = 44.0 Hz, SiCH<sub>2</sub>), 109.2, 116.8, 139.1, 141.4, 163.2<sup>29</sup>Si -22.3 (d, <sup>1</sup>J<sub>SiF</sub> = 256.8 Hz)Massm/z: 185 (M<sup>+</sup>), 184, 170, 166AnalysisFound: C, 51.60; H, 6.51; N, 7.45. C<sub>8</sub>H<sub>12</sub>NOFSi

calcd.: C, 51.86; H, 6.53; N, 7.56

ii) Fluorodimethylsilylmethyl-6-methylpyrid-2-one (2.7B, Y = 6-Me)

Chlorodimethylsilylmethyl-6-methylpyrid-2-one 1.08 g

SbF<sub>3</sub> 0.31 g

Yield 0.61 g, 91%

M.P. 87-89°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.28 (d, <sup>3</sup>J<sub>HSiF</sub> = 5.9 Hz, 6H, SiMe<sub>2</sub>), 2.5 (s, 3H, Me), 3.0 (s, 2H, NCH<sub>2</sub>), 6.5-7.5 (m, 3H, arom)<sup>13</sup>C 2.4 (d, <sup>2</sup>J<sub>CSiF</sub> = 27.2 Hz, SiMe), 20.9, 35.8 (d, <sup>2</sup>J<sub>CSiF</sub> = 50.5 Hz, SiCH<sub>2</sub>), 110.2, 112.5, 141.2, 148.6, 163.8<sup>29</sup>Si -35.5 (d, <sup>1</sup>J<sub>SiF</sub> = 252.9 Hz)



AnalysisFound: C, 54.26; H, 7.11; N, 6.96.  $C_9H_{14}NOFSi$ 

calcd.: C, 54.24; H, 7.08; N, 7.03

iii) Fluorodimethylsilylmethyl-3-methoxypyrid-2-one (2.7B, Y= 3-OMe)

Chlorodimethylsilylmethyl-3-methoxypyrid-2-one 1.16 g

SbF<sub>3</sub> 0.31 g

Yield 0.66 g, 92%

M.P. 88-92°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.35 (d, <sup>3</sup>J<sub>HSiF</sub>= 5.1 Hz, 6H, SiMe<sub>2</sub>), 3.3 (s, 2H, NCH<sub>2</sub>), 3.9 (s, 3H, OMe), 6.2-6.4 (m, 3H, arom)<sup>13</sup>C 1.4 (d, <sup>2</sup>J<sub>CSiF</sub>= 23.3 Hz, SiMe), 40.2 (d, <sup>2</sup>J<sub>CSiF</sub>= 40.2 Hz, SiCH<sub>2</sub>), 56.1, 107.7, 114.6, 129.7, 148.3, 158.3<sup>29</sup>Si -13.5 (d, <sup>1</sup>J<sub>SiF</sub>= 258.8 Hz)AnalysisFound: C, 50.02; H, 6.64; N, 6.39.  $C_9H_{14}NO_2FSi$ 

calcd.: C, 50.21; H, 6.55; N, 6.51

iv) Fluorodimethylsilylmethyl-5-chloropyrid-2-one (2.7B, Y= 5-Cl)

Chlorodimethylsilylmethyl-5-chloropyrid-2-one 1.18 g

SbF<sub>3</sub> 0.31 g

Yield 0.66 g, 90%

M.P. 91-95°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.31 (d, <sup>3</sup>J<sub>CSiF</sub>=7.8 Hz, 6H, SiMe<sub>2</sub>), 3.2 (s, 2H, NCH<sub>2</sub>), 6.7-7.7 (m, 3H, arom)<sup>13</sup>C 1.2 (d, <sup>2</sup>J<sub>CSiF</sub>= 19.4 Hz, SiMe), 40.4 (d, <sup>2</sup>J<sub>CSiF</sub>= 41.4 Hz, SiCH<sub>2</sub>), 115.0, 118.0, 137.0, 142.1, 161.9<sup>29</sup>Si -14.6 (d, <sup>1</sup>J<sub>SiF</sub>= 259.8 Hz)Massm/z: 219/221 (3:1, M<sup>+</sup>), 218/220 (3:1), 204/206 (3:1), 184AnalysisFound: C, 43.26; H, 5.00; N, 6.07. C<sub>8</sub>H<sub>11</sub>NOFCISi  
calcd.: C, 43.73; H, 5.05; N, 6.37v) Fluorodimethylsilylmethyl-3-nitropyrid-2-one (2.7B, Y=3-NO<sub>2</sub>)

Chlorodimethylsilylmethyl-3-nitropyrid-2-one 1.23 g

SbF<sub>3</sub> 0.31 g

Yield 0.69 g, 90%

M.P. 87-90°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.38 (d, <sup>3</sup>J<sub>CSiF</sub>= 7.8 Hz, 6H, SiMe<sub>2</sub>), 3.6 (s, 2H, NCH<sub>2</sub>), 6.4-8.4 (m, 3H, arom)<sup>13</sup>C -0.52 (d, <sup>2</sup>J<sub>CSiF</sub>= 18.1 Hz, SiMe), 42.7 (d, <sup>2</sup>J<sub>CSiF</sub>= 29.8 Hz, SiCH<sub>2</sub>), 105.1, 137.4, 139.0, 145.9, 155.6.<sup>29</sup>Si 12.5 (d, <sup>1</sup>J<sub>SiF</sub>= 272.5 Hz)

AnalysisFound: C, 42.01; H, 4.95; N, 11.83.  $C_8H_{11}N_2O_3FSi$ 

calcd.: C, 41.72; H, 4.82; N, 12.17

vi) Fluorodimethylsilylmethyl-6-chloropyrid-2-one (2.7B, Y=6-Cl)

Chlorodimethylsilylmethyl-6-chloropyrid-2-one 1.18 g

 $SbF_3$  0.31 g

Yield 0.68 g, 92%

M.P. 90-95°C

NMR $\delta$ / ppm ( $CDCl_3$ , TMS) $^1H$  0.31 (brs, 6H,  $SiMe_2$ ), 3.2 (s, 2H,  $NCH_2$ ),

6.6-7.6 (m, 3H, arom)

 $^{13}C$  1.9 (d,  $^2J_{CSiF} = 19.4$  Hz,  $SiMe$ ), 38.0 (d, $^2J_{CSiF} = 46.6$  Hz,  $SiCH_2$ ), 109.8, 114.3, 140.4,

141.0, 164.1

 $^{29}Si$  -26.0 (d,  $^1J_{SiF} = 257.8$  Hz)Mass $m/z$ : 219/221 (3:1,  $M^+$ ), 218/220 (3:1), 204/206

(3:1), 184

AnalysisFound: C, 43.10; H, 5.00; N, 6.21.  $C_8H_{11}NOCIFSi$ 

calcd.: C, 43.73; H, 5.05; N, 6.37

Preparation of chloromethyldimethylsilyltriflate (ClCH<sub>2</sub>SiMe<sub>2</sub>OTf) (2.3B, X=OTf)

5 ml (37.8 mmol) trifluoromethanesulphonic acid was added to 3.34 ml (37.8 mmol) chloromethyldimethylchlorosilane, with stirring under nitrogen. The reaction

mixture was heated at 60°C for 5 hrs. and finally the product was isolated by distillation.

B.P. 62°C/ 8 mm Hg

Yield 8.62 g, 89%

NMR

$\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.60 (s, 6H, SiMe<sub>2</sub>), 3.0 (s, 2H; CH<sub>2</sub>)

<sup>13</sup>C -3.0, 27.6, 118.9 (q, <sup>1</sup>J<sub>CF</sub> = 317.1 Hz, CF<sub>3</sub>)

<sup>29</sup>Si 31.7

Mass

m/z: 256/258 (3:1), 207, 191

Analysis

Found: C, 17.95; H, 3.13. C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>ClF<sub>3</sub>SSi calcd.:

C, 18.71; H, 3.15

**GENERAL PROCEDURE FOR THE SYNTHESIS OF SILYL TRIFLATE DERIVATIVES FROM SILYLATED PYRIDONES AND CHLOROMETHYLDIMETHYLSILYLTRIFLATE**

The procedure was the same as for the synthesis of five coordinate silyl chlorides. Chloromethyldimethylchlorosilane was replaced by chloromethyldimethylsilyl-triflate.

i) Dimethylsilylmethylpyrid-2-one triflate (2.4Bb, Y=H)

2-Trimethylsiloxypyridine 0.38 g, 2.28 mmol

Chloromethyldimethylsilyltriflate 0.59 g, 2.28 mmol

Yield 0.63 g, 88%

M.P. 120-123°C

NMR $\delta$ / ppm (CD<sub>3</sub>CN, TMS)<sup>1</sup>H 0.66 (s, 6H, SiMe<sub>2</sub>), 4.0 (s, 2H, NCH<sub>2</sub>),

7.2-8.3 (m, 4H, arom)

<sup>13</sup>C 0.17, 42.8, 115.2, 118.3, 142.3, 147.5, 162.9<sup>29</sup>Si 32.3AnalysisFound: C, 32.76; H, 3.81; N, 4.50. C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>F<sub>3</sub>NSSi

calcd.: C, 34.27; H, 3.84; N, 4.42

ii) Dimethylsilylmethyl-6-methylpyrid-2-one triflate (2.4Bb, Y=6-Me)

2-Trimethylsiloxy-6-methylpyridine 0.42 g, 2.32 mmol

Chloromethyldimethylsilyltriflate 0.60 g, 2.32 mmol

Yield 0.69 g, 90%

M.P. 128-132°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>+CD<sub>3</sub>CN, 1:1, TMS)<sup>1</sup>H 0.64 (s, 6H, SiMe<sub>2</sub>), 2.6 (s, 3H, Me), 3.8 (s, 2H, NCH<sub>2</sub>), 7.0-8.1 (m, 3H, arom)<sup>13</sup>C 3.2, 20.5, 39.8, 111.5, 117.9, 121.0 (q, <sup>1</sup>J<sub>CF</sub>= 321.0 Hz, CF<sub>3</sub>), 146.1, 152.7, 163.0<sup>29</sup>Si 23.0AnalysisFound: C, 36.52; H, 4.48; N, 4.80. C<sub>10</sub>H<sub>14</sub>NSF<sub>3</sub>O<sub>4</sub>Si

calcd.: C, 36.46; H, 4.28; N, 4.25

iii) Dimethylsilylmethyl-3-methoxypyrid-2-one triflate (2.4Bb, Y=3-OMe)

2-Trimethylsiloxy-3-methoxypyridine 0.76 g, 3.86 mmol

Chloromethyldimethylsilyltriflate 0.99 g, 3.86 mmol

Yield. 1.13 g, 85%

M.P. 127-130°C

NMR

$\delta$ / ppm ( $\text{CDCl}_3$ , TMS)

$^1\text{H}$  0.69 (s, 6H,  $\text{SiMe}_2$ ), 3.9 (s, 3H, OMe), 4.0 (s, 2H,  $\text{NCH}_2$ ), 7.1-7.9 (m, 3H, arom)

$^{13}\text{C}$  3.1, 42.9, 57.2, 116.9, 120.3 (q,  $^1J_{\text{CF}} = 319.2$  Hz,  $\text{CF}_3$ ), 123.5, 131.3, 146.5, 155.8

$^{29}\text{Si}$  21.3

Analysis

Found: C, 33.92; H, 3.92; N, 4.10.  $\text{C}_{10}\text{H}_{14}\text{NSF}_3\text{O}_5\text{Si}$

calcd.: C, 34.78; H, 4.09; N, 4.06

iv) Dimethylsilylmethyl-5-chloropyrid-2-one triflate (2.4Bb, Y=5-Cl)

2-Trimethylsiloxy-5-chloropyridine 0.48 g, 2.39 mmol

Chloromethyldimethylsilyltriflate 0.61 g, 2.39 mmol

Yield 0.74 g, 88%

M.P. 136-139°C

NMR

$\delta$ / ppm ( $\text{CDCl}_3 + \text{CD}_3\text{CN}$  1:1, TMS)

$^1\text{H}$  0.67 (s, 6H,  $\text{SiMe}_2$ ), 4.0 (s, 2H,  $\text{NCH}_2$ ), 7.1-8.3 (m, 3H, arom)

$^{13}\text{C}$  1.7, 41.5, 115.8, 118.8 (q,  $^1J_{\text{CF}} = 319.7$  Hz,  $\text{CF}_3$ ), 123.9, 139.6, 147.0, 161.8

$^{29}\text{Si}$  25.2

Mass  $m/z$ : 349/351 (3:1,  $M^+$ ), 334/336 (3:1), 200/202 (3:1),

Analysis Found: C, 31.02; H, 3.32; N, 4.27.  $C_9H_{11}O_4F_3ClN_2SSi$   
calcd.: C, 30.90; H, 3.17; N, 4.00

v) Dimethylsilylmethyl-3-nitropyrid-2-one triflate (2.4Bb, Y = 3-NO<sub>2</sub>)

2-Trimethylsiloxy-3-nitropyridine 0.53 g, 2.5 mmol

Chloromethyldimethylsilyltriflate 0.64 g, 2.5 mmol

Yield 0.80 g, 89%

M.P. 129-131°C

NMR  $\delta$ / ppm ( $CDCl_3 + CD_3CN$ , 1:1, TMS)  
 $^1H$  0.66 (s, 6H, SiMe<sub>2</sub>), 4.0 (s, 2H, NCH<sub>2</sub>),  
7.2-8.8 (m, 3H, arom)  
 $^{13}C$  3.2, 42.1, 114.8, 120.3 (q,  $^1J_{CF}$  = 319.4 Hz,  
CF<sub>3</sub>), 135.5, 142.4, 147.4, 158.0  
 $^{29}Si$  4.5

Analysis Found: C, 29.96; H, 3.64; N, 8.86.  $C_9H_{11}O_6F_3N_2SSi$   
calcd.: C, 30.0; H, 3.08; N, 7.78

vi) Dimethylsilylmethyl-6-chloropyrid-2-one triflate (2.4Bb, Y = 6-Cl)

2-Trimethylsiloxy-6-chloropyridine 0.80 g, 3.98 mmol

Chloromethyldimethylsilyltriflate 1.02 g, 3.98 mmol

Yield 1.28 g, 92%

M.P. 135-140°C

NMR $\delta$ / ppm ( $\text{CDCl}_3 + \text{CD}_3\text{CN}$ , 1:1, TMS) $^1\text{H}$  0.65 (s, 6H,  $\text{SiMe}_2$ ), 3.9 (s, 2H,  $\text{NCH}_2$ ),

7.2-8.0 (m, 3H, arom)

 $^{13}\text{C}$  1.7, 41.8, 112.8, 116.8, 120.3 (q,  $^1J_{\text{CF}} = 319.7$  Hz), 142.8, 146.5, 165 $^{29}\text{Si}$  10.7Mass $m/z$ : 349/351 (3:1,  $\text{M}^+$ ), 334/336 (3:1), 200/202 (3:1)AnalysisFound: C, 31.56; H, 3.21; N, 4.49.  $\text{C}_9\text{H}_{11}\text{O}_4\text{F}_3\text{ClNSSi}$   
calcd.: C, 30.90; H, 3.17; N, 4.00**GENERAL PROCEDURE FOR THE SYNTHESIS OF DISILOXANE****(2.14B)**

0.5 g of chloro silyl pyridone (**2.4Ba**) was added to 1 ml distilled water and the reaction mixture was stirred for 1 hr and then extracted with chloroform (3x75 ml). The washed extract was dried over anhydrous magnesium sulphate and distilled under reduced pressure and dried under vacuum. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR data of disiloxanes are shown in Tables 2.1B-2.6B.

**GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE  
SILYL DICHLORIDES FROM SILYLATED PYRIDONES AND  
CHLOROMETHYLDICHLOROMETHYLSILANE**

Chloromethyldichloromethylsilane in dry hexane was added slowly into a stirred solution of 2-trimethylsiloxypyridine (both are equimolar amounts) in dry hexane



under nitrogen. The reaction mixture was stirred for 7 hrs. and the solid obtained was filtered under nitrogen and dried under vacuum.

i) Dichloromethylsilylmethylpyrid-2-one (2.8B, Y=H)

2-Trimethylsiloxypyridine 0.53 g, 3.17 mmol

Chloromethyldichloromethylsilane 404  $\mu$ l, 3.17 mmol

Yield 0.62 g, 88%

M.P. 107-111°C

NMR

$\delta$ / ppm ( $\text{CDCl}_3 + \text{CD}_3\text{CN}$ , 1:1, TMS)

$^1\text{H}$  0.95 (s, 3H, SiMe), 3.9 (s, 2H,  $\text{NCH}_2$ ),  
6.9-8.0 (m, 4H, arom)

$^{13}\text{C}$  11.9, 44.0, 113.9, 114.5, 139.0, 144.8, 162.2

$^{29}\text{Si}$  -52.5 (sbr)

Mass

m/z: 221/223/225 (10:6:1,  $\text{M}^+$ ), 220/222/224

(10:6:1), 206/208/210 (10:6:1), 186/188 (3:1),

151.

Analysis

Found: C, 37.95; H, 4.36; N, 6.31.  $\text{C}_7\text{H}_9\text{NOCl}_2\text{Si}$

calcd.: C, 37.85; H, 4.08; N, 6.31

ii) Dichloromethylsilylmethyl-3-methoxypyrid-2-one (2.8B, Y= 3-OMe)

2-Trimethylsiloxy-3-methoxypyridine 0.72 g, 3.65 mmol

Chloromethyldichloromethylsilane 465  $\mu$ l, 3.65 mmol

Yield 0.85 g,

M.P. 108-111°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.92 (s, 3H, SiMe), 3.2 (s, 2H, NCH<sub>2</sub>), 3.9 (s, 3H, OMe), 6.9-7.6 (m, 3H, arom)<sup>13</sup>C 12.2, 44.4, 56.8, 112.8, 119.7, 128.7, 146.3, 156.4<sup>29</sup>Si -50.0Massm/z: 251/253/255 (10:6:1, M<sup>+</sup>), 236/238/240 (10:6:1), 216/218 (3:1), 181AnalysisFound: C, 37.57; H, 4.60; N, 5.40. C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>Cl<sub>2</sub>Si  
calcd.: C, 38.10; H, 4.40; N, 5.55iii) Dichloromethylsilylmethyl-5-chloropyrid-2-one (2.8B, Y= 5-Cl)

2-Trimethylsiloxy-5-chloropyridine 0.66 g, 3.28 mmol

Chloromethyldichloromethylsilane 417  $\mu$ l, 3.28 mmol

Yield 0.76 g, 91%

M.P. 114-119°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)<sup>1</sup>H 0.97 (s, 3H, SiMe), 3.8 (s, 2H, NCH<sub>2</sub>), 6.9-7.9 (m, 3H, arom)<sup>13</sup>C 10.0, 44.3, 115.6, 119.8, 136.3, 144.8, 161.1<sup>29</sup>Si -50.2 (sbr)Massm/z: 255/257/259/261 (10:9.6:3:1, M<sup>+</sup>), 240/242/244/246 (10:9.6:3:1), 220/222/224 (10:6:1), 185/187 (3:1)

AnalysisFound: C, 32.59; H, 3.40; N, 5.30.  $C_7H_8NOCl_3Si$ 

calcd.: C, 32.77; H, 3.14; N, 5.46

iv) Dichloromethylsilylmethyl-6-chloropyrid-2-one (2.8B, Y= 6-Cl)

2-Trimethylsiloxy-6-chloropyridine 0.58 g, 2.88 mmol

Chloromethyldichloromethylsilane 367  $\mu$ l, 2.88 mmol

Yield 0.66 g, 90%

M.P. 115-117°C

NMR $\delta$ / ppm ( $CDCl_3$ , TMS) $^1H$  0.98 (s, 3H, SiMe), 3.8 (s, 2H,  $NCH_2$ ),

6.9-7.9 (m, 3H, arom)

 $^{13}C$  12.0, 43.1, 112.5, 113.9, 140.3, 144.2, 163.3 $^{29}Si$  -52.3 (sbr)AnalysisFound: C, 33.18; H, 3.39; N, 5.45.  $C_7H_8NOCl_3Si$ 

calcd.: C, 32.77; H, 3.14; N, 5.46

GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE  
SILYL DIFLUORIDES (2.10B) FROM FIVE COORDINATE SILYL  
DICHLORIDES AND ANTIMONY TRIFLUORIDE

3 mmol of pentacoordinate silyl dichloride (2.8B) was dissolved (or suspended) in 5 ml dry benzene under nitrogen. 2 mmol of antimony trifluoride was added to it and the reaction mixture was stirred for 0.5 hr.. It was then diluted with water and extracted with chloroform (3 x 75 ml). The extract was dried over anhydrous

magnesium sulphate and distilled and dried under vacuum to yield a colourless crystalline solid.

i) Difluoromethylsilylmethylpyrid-2-one (2.10B, Y=H)

Dichloromethylsilylmethylpyrid-2-one 0.66 g

SbF<sub>3</sub> 0.36 g

Yield 0.43 g, 91%

M.P. 95-102°C

NMR

δ/ ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.39 (t, <sup>3</sup>J<sub>HSiF</sub>= 5.1 Hz, 3H, SiMe), 3.3 (s, 2H, NCH<sub>2</sub>), 6.7-7.8 (m, 4H, arom)

<sup>13</sup>C 1.0 (t, <sup>2</sup>J<sub>CSiF</sub>= 20.7 Hz, SiMe), 37.3 (t, <sup>2</sup>J<sub>CSiF</sub>= 32.4 Hz, SiCH<sub>2</sub>), 111.9, 115.6, 138.9, 143.3, 163.2

<sup>29</sup>Si -59.9 (t, <sup>1</sup>J<sub>SiF</sub>= 253.9 Hz, SiF)

Mass

m/z: 189 (M<sup>+</sup>), 188, 174, 170

Analysis

Found: C, 43.22; H, 5.03; N, 6.87. C<sub>7</sub>H<sub>9</sub>NOF<sub>2</sub>Si

calcd.: C, 44.43; H, 4.79; N, 7.40

ii) Difluoromethylsilylmethyl-3-methoxypyrid-2-one (2.10B, Y= 3-OMe)

Dichloromethylsilylmethyl-3-methoxypyrid-2-one 0.75 g

SbF<sub>3</sub> 0.36 g

Yield 0.51 g, 93%

M.P. 99-106°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.47 (t, <sup>3</sup>J<sub>HSiF</sub>= 5.3 Hz, 3H, SiMe), 3.3 (s, 2H, NCH<sub>2</sub>), 3.9 (s, 3H, OMe), 6.5-7.4 (m, 3H, arom)

<sup>13</sup>C 0.86 (t, <sup>2</sup>J<sub>CSiF</sub>= 23.3 Hz, SiMe), 37.5 (t, <sup>2</sup>J<sub>CSiF</sub>= 33.7 Hz, SiCH<sub>2</sub>), 56.4, 110.4, 117.2, 128.3, 147.0, 157.8

<sup>29</sup>Si -57.1 (t, <sup>1</sup>J<sub>SiF</sub>= 256.8 Hz, SiF)

Mass

m/z: 219 (M<sup>+</sup>), 218, 204, 200, 188

Analysis

Found: C, 42.99; H, 5.20; N, 5.90. C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>F<sub>2</sub>Si  
calcd.: C, 43.82; H, 5.06; N, 6.39

iii) Difluoromethylsilylmethyl-5-chloropyrid-2-one (2.10B, Y= 5-Cl)

Dichloromethylsilylmethyl-5-chloropyrid-2-one 0.77 g

SbF<sub>3</sub> 0.36 g

Yield 0.50 g, 89%

M.P. 102-105°C

NMR $\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.40 (t, <sup>3</sup>J<sub>HSiF</sub>= 5.4 Hz, 3H, SiMe), 3.3 (s, 2H, NCH<sub>2</sub>), 6.7-7.8 (m, 3H, arom)

<sup>13</sup>C 0.63 (t, <sup>2</sup>J<sub>CSiF</sub>= 22.0 Hz, SiMe), 37.7 (t, <sup>2</sup>J<sub>CSiF</sub>=32.4 Hz, SiCH<sub>2</sub>), 116.5, 117.9, 136.3, 143.6, 161.8

<sup>29</sup>Si -57.2 (t, <sup>1</sup>J<sub>SiF</sub>= 255.9 Hz, SiF)

Mass  $m/z$ : 223/225 (3:1,  $M^+$ ), 222/224 (3:1), 208/210 (3:1), 204/206 (3:1), 188

Analysis Found: C, 37.88; H, 3.86; N, 6.12.  $C_7H_8NOClF_2Si$   
calcd.: C, 37.59; H, 3.60; N, 6.26

iv) Difluoromethylsilylmethyl-6-chloropyrid-2-one (2.10B, Y= 6-Cl)

Dichloromethylsilylmethyl-6-chloropyrid-2-one 0.77 g

$SbF_3$  0.36 g

Yield 0.51 g, 91%

M.P. 102-104°C

NMR  $\delta$ / ppm ( $CDCl_3$ , TMS)  
 $^1H$  0.41 (t,  $^3J_{HSiF} = 5.5$  Hz, 3H, SiMe), 3.3 (s, 2H,  $NCH_2$ ), 6.8-7.7 (m, 3H, arom)  
 $^{13}C$  0.75 (t,  $^2J_{CSiF} = 23.3$  Hz, SiMe), 36.4 (t,  $^2J_{CSiF} = 35.0$  Hz,  $SiCH_2$ ), 111.9, 113.1, 140.6, 142.7, 164.1  
 $^{29}Si$  -60.4 (t,  $^1J_{SiF} = 253.9$  Hz, SiF)

Mass  $m/z$ : 223/225 (3:1,  $M^+$ ), 222/224 (3:1), 208/210 (3:1), 188

Analysis Found: C, 36.29; H, 3.87; N, 5.61.  $C_7H_8NOClF_2Si$   
calcd.: C, 37.59; H, 3.60; N, 6.26

**GENERAL PROCEDURE FOR THE SYNTHESIS OF FIVE COORDINATE TRICHLORO SILYL DERIVATIVES (2.9B) FROM SILYLATED PYRIDONES AND CHLOROMETHYLTRICHLOROSILANE**

Chloromethyltrichlorosilane in dry hexane was added slowly into a stirred solution of 2-trimethylsiloxypyridine (both are equimolar amounts) in dry hexane under nitrogen. The reaction mixture was stirred for overnight and the solid obtained was filtered under nitrogen and dried under vacuum.

**i) Trichlorosilylmethylpyrid-2-one (2.9B, Y=H)**

2-Trimethylsiloxypyridine 0.53 g, 3.17 mmol

Chloromethyltrichlorosilane 395  $\mu$ l, 3.17 mmol

Yield 0.71 g, 92%

M.P. 125-130°C

**NMR**

$\delta$ / ppm (CDCl<sub>3</sub>+CD<sub>3</sub>CN, 1:1, TMS)

<sup>1</sup>H 4.1 (s, 2H, NCH<sub>2</sub>), 7.0-8.1 (m, 4H, arom)

<sup>13</sup>C 44.2, 114.0, 115.4, 140.0, 146.1, 160.8,

<sup>29</sup>Si -77.7 (sbr)

**Mass**

m/z: 241/243/245/247 (30:29:9:1, M<sup>+</sup>), 206/208/210  
(10:6:1), 171/173 (3:1), 157, 136

**Analysis**

Found: C, 30.30; H, 3.26; N, 5.73. C<sub>6</sub>H<sub>6</sub>NOCl<sub>3</sub>Si  
calcd.: C, 29.71; H, 2.69; N, 5.77

ii) Trichlorosilylmethyl-6-methylpyrid-2-one (2.9B, Y= 6-Me)

2-Trimethylsiloxy-6-methylpyridine 0.42 g, 2.32 mmol

Chloromethyltrichlorosilane 289  $\mu$ l, 2.32 mmol

Yield 0.54 g, 91%

M.P. 129-136°C

NMR

$\delta$ / ppm ( $\text{CD}_3\text{CN}+2$  drops  $\text{DMSO}-d_6$ , TMS)

$^1\text{H}$  2.7 (s, 3H, Me), 4.0 (s, 2H,  $\text{NCH}_2$ ), 6.9-8.2 (m, 3H, arom)

$^{13}\text{C}$  21.1, 39.0, 111.6, 117.4, 146.0, 152.0, 162.1

$^{29}\text{Si}$  -89.7 (sbr)

Mass

m/z: 255/257/259/261 (30:29:9:1,  $\text{M}^+$ ), 240/242/244/246 (30:29:9:1), 220/224/226 (10:6:1), 185/187 (3:1), 150

Analysis

Found: C, 26.72; H, 3.46; N, 4.43.  $\text{C}_7\text{H}_8\text{NOCl}_3\text{Si}$   
calcd.: C, 32.77; H, 3.14; N, 5.46

iii) Trichlorosilylmethyl-6-chloropyrid-2-one (2.9B, Y= 6-Cl)

2-Trimethylsiloxy-6-chloropyridine 0.50 g, 2.48 mmol

Chloromethyltrichlorosilane 309  $\mu$ l, 2.48 mmol

Yield 0.62 g, 90%

M.P. 131-134°C

NMR

$\delta$ / ppm ( $\text{CDCl}_3$ , TMS)

$^1\text{H}$  4.0 (s, 2H,  $\text{NCH}_2$ ), 6.9-7.9 (m, 3H, arom)



$^{13}\text{C}$  43.8, 111.9, 115.1, 140.6, 145.0, 162.5

$^{29}\text{Si}$  -85.6 (sbr)

Mass

m/z: 275/277/279/281/283 (95:122:59:12:1,  $\text{M}^+$ ),

240/242/244/246 (30:29:9:1), 205/207/209

(10:6:1), 170/172 (3:1), 158/160 (3:1), 135

Analysis

Found: C, 28.16; H, 2.89; N, 5.63.  $\text{C}_6\text{H}_5\text{NOCl}_4\text{Si}$

calcd.: C, 26.02; H, 1.82; N, 5.06

### CONDUCTIVITY:

Conductivity measurements were carried out using a PTI-10 digital conductivity meter (quoted  $\pm 0.5$  %, repeatability  $\pm 1$  digit); all experiments were performed under nitrogen. Calibration of the meter was checked by using a standard solution of potassium chloride.

The compound whose conductivity is to be determined was dissolved in acetonitrile and introduced into the cell by a syringe. The conductivity of the following solutions were measured.

$n\text{Bu}_4\text{NBr}$  (0.23 g, 7 ml,  $\text{CH}_3\text{CN}$ , 0.1 M solution)  $182 \mu\text{S cm}^{-1}$ .

(2.1B) (X=Br, Y=H) (0.17 g, 7 ml,  $\text{CH}_3\text{CN}$ , 0.1 M solution)  $008 \mu\text{S cm}^{-1}$ .

(2.1B) (X=OTf, Y=H) (0.22 g, 7 ml,  $\text{CH}_3\text{CN}$ , 0.1 M solution)  $029 \mu\text{S cm}^{-1}$ .

### Reaction of halodimethylsilylmethylpyrid-2-one (2.1B, X=F, Cl, Br Y=H) with nucleophiles (e.g. NMI, HMPA)

Reaction of fluoro, chloro and bromo pyridones (2.1B, X= F, Cl, Br Y=H) towards different nucleophiles have shown that chloro and bromo derivatives undergo substitution (Tables 2.1A and 2.7B) while fluoroderivative was found to be unreactive (Tables 2.8B-2.9B)

**GENERAL PROCEDURE FOR THE SYNTHESIS OF N, N-BIS(HALO-DIMETHYLSILYLMETHYL)ACETAMIDE<sup>146</sup>**

N,O-bis(trimethylsilyl)acetamide (4.05 mmols) was added slowly with stirring to a solution of halomethyldimethylchlorosilane (8.09 mmols) in 5 ml dry hexane under nitrogen. The process is exothermic and the reaction flask was cooled in ice during the addition. After 2 hrs. precipitated bis(halodimethylsilylmethyl)acetamide was filtered off, washed with hexane, and dried under reduced pressure.

i) Bis(chlorodimethylsilylmethyl)acetamide (3.7, X=Cl)

Bis(trimethylsilyl)acetamide 1 ml

Chloromethyldimethylchlorosilane 1.07 ml

Yield 1.32 g, 80%

M.P. 123-125°C (Lit<sup>146</sup>, 128-131°C)

NMR

$\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.56 (s, 6H, MeSi<sup>a</sup>), 0.61 (s, 6H, MeSi<sup>b</sup>), 2.2 (s, 3H, C-Me), 2.8 (s, 2H, CH<sub>2</sub>Si<sup>b</sup>), 3.3 (s, 2H, CH<sub>2</sub>Si<sup>a</sup>)

<sup>13</sup>C 1.9, 7.4, 17.6, 42.6, 44.6, 173.1

<sup>29</sup>Si 26.8 (Si<sup>a</sup>); -39.9 (Si<sup>b</sup>)

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

ii) Bis(bromodimethylsilylmethyl)acetamide (3.7, X=Br)

Bis(trimethylsilyl)acetamide 1 ml

Bromomethyldimethylchlorosilane 1.10 ml

Yield 1.75 g, 80%

M.P. 149-151°C (Lit<sup>146</sup>. 150-151°C)

NMR

$\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.73 (s, 6H, MeSi<sup>a</sup>), 0.83 (s, 6H, MeSi<sup>b</sup>),  
2.3 (s, 3H, C-Me), 3.2 (s, 2H, CH<sub>2</sub>Si<sup>b</sup>), 3.6 (s,  
2H, CH<sub>2</sub>Si<sup>a</sup>)

<sup>13</sup>C 2.4, 6.8, 17.9, 43.0, 46.4, 174.6

<sup>29</sup>Si 26.0 (Si<sup>a</sup>); -13.8 (Si<sup>b</sup>)

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

Preparation of bis(fluorodimethylsilylmethyl)acetamide (3.8)

3 mmols (0.82 g) of bis(chlorodimethylsilylmethyl)acetamide (3.7, X=Cl) was dissolved in 5 ml dry benzene under nitrogen. 2 mmols (0.36 g) of antimony trifluoride was added to it and the reaction mixture was stirred for 0.5 hr. and then diluted with water and extracted with chloroform (3 x 75 ml). The washed extract was dried over anhydrous magnesium sulphate, distilled under reduced pressure and finally dried under vacuum.

Yield 0.51 g, 85%

M.P. 110-112°C

NMR

$\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.23 (d, <sup>3</sup>J<sub>HSiF</sub> = 7.6 Hz, 6H, MeSi<sup>a</sup>), 0.37 (d,  
<sup>3</sup>J<sub>HSiF</sub> = 7.6 Hz, MeSi<sup>b</sup>), 2.1 (s, 3H, C Me),

2.4 (s, 2H, CH<sub>2</sub>Si<sup>b</sup>), 3.1 (d, <sup>3</sup>J<sub>HSiF</sub> = 6.6 Hz,

2H, CH<sub>2</sub>Si<sup>a</sup>)

<sup>13</sup>C -1.8 (d, <sup>2</sup>J<sub>CSiF</sub> = 14.2 Hz, MeSi<sup>a</sup>), 1.8 (d,

<sup>2</sup>J<sub>CSiF</sub> = 24.6 Hz, MeSi<sup>b</sup>), 18.3, 39.4, 41.7 (d,

<sup>2</sup>J<sub>CSiF</sub> = 18.1 Hz), 171.2

<sup>29</sup>Si 28.9 (d, <sup>1</sup>J<sub>SiF</sub> = 287.1 Hz, MeSi<sup>a</sup>)

-23.5 (d, <sup>1</sup>J<sub>SiF</sub> = 256.8 Hz, MeSi<sup>b</sup>)

### Analysis

Found: C, 40.31; H, 8.15; N, 5.85. C<sub>8</sub>H<sub>19</sub>ONCl<sub>2</sub>Si<sub>2</sub>

calcd.: C, 40.14; H, 8.00; N, 5.85

<sup>a</sup>Four coordinate silicon atom; <sup>b</sup>Five coordinate silicon atom

### Preparation of chlorodimethylsilylmethyl-N-methylacetamide<sup>172</sup>

N-Methyltrimethylsilylacetamide (900 μl, 5.6 mmol) was added slowly with stirring to a solution of chloromethyldimethylchlorosilane (741 μl, 5.6 mmols) in 5 ml dry ether under nitrogen. After 1 hr. precipitated chlorodimethylsilylmethyl-N-methylacetamide was filtered off, washed with dry ether, and dried under reduced pressure.

Yield 0.80 g, 80%

M.P. 65-67°C (Lit<sup>172</sup>. 64°-66°C)

### NMR

δ/ ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.48 (s, 6H, SiMe), 2.1 (s, 3H, C-Me), 2.8 (s, 2H, NCH<sub>2</sub>), 3.1 (s, 3H, NCH<sub>3</sub>)

<sup>13</sup>C 7.0, 17.3, 37.4, 43.9, 173.7

<sup>29</sup>Si -38.7

Preparation of fluorodimethylsilylmethyl-N-methyl acetamide (3.13)

4.46 mmol (0.80 g) of chlorodimethylsilylmethyl-N-methylacetamide was suspended in 5 ml dry benzene under nitrogen. 1.49 mmol (0.27 g) of antimony trifluoride was added to it and the reaction mixture was stirred for 0.5 hr.. It was then diluted with water and extracted with chloroform (3 x 75 ml). The washed extract was dried over anhydrous magnesium sulphate and distilled under reduced pressure and dried under vacuum to yield a colourless crystalline solid.

Yield 0.44 g, 91%

M.P. 56-57°C

NMR

$\delta$ / ppm (CDCl<sub>3</sub>, TMS)

<sup>1</sup>H 0.22 (d, <sup>3</sup>J<sub>HF</sub> = 7.8 Hz, 6H, MeSi), 2.1 (s, 3H, C-Me), 2.4 (s, 2H, CH<sub>2</sub>Si), 3.1 (s, 3H, NMe)

<sup>13</sup>C 1.7 (d, <sup>2</sup>J<sub>CF</sub> = 20.7 Hz), 18.3, 37.8, 39.7 (d, <sup>2</sup>J<sub>CF</sub> = 40.1 Hz, CH<sub>2</sub>Si), 171.7

<sup>29</sup>Si -21.2 (d, <sup>1</sup>J<sub>SiF</sub> = 258.8 Hz)

Mass

m/z: 163 (M<sup>+</sup>), 148, 144

## GENERAL PROCEDURE FOR THE SYNTHESIS OF HEXACOORDINATED ORGANOSILYLAMIDES

2.5 mmol of dichloromethyl(methyldichloro)silane in dry ether was added slowly into a stirred solution of 2-trimethylsiloxypyridine (5 mmol) in dry ether under nitrogen. The reaction mixture was stirred for 48 hrs. and the solid obtained was filtered under nitrogen and dried under vacuum.

### i) Dichloromethylsilylmethyl bis(6-methylpyrid-2-one) (4.6a)

2-Trimethylsiloxy-6-methylpyridine 0.91 g

Dichloromethyl(methyldichloro)silane 350  $\mu$ l

Yield 1.16 g, 90%

M.P. 178-182°C

<u>N.M.R.</u>	$\delta$ / ppm (CDCl <sub>3</sub> , TMS)
<sup>1</sup> H	0.94 (s, 3H, SiMe), 2.7 (s, 3H, CH <sub>3</sub> ), 5.3 (s, 1H, CHSi), 6.7-7.9 (m, 6H, arom)
<sup>13</sup> C	3.2, 21.5, 68.4, 113.6, 115.5, 145.0, 150.3, 165.9
<sup>29</sup> Si	-120.4
<u>Mass</u>	m/z: 342/344/346 (10:6:1, M <sup>+</sup> ), 327/329/331 (10:6:1), 307/309 (3:1), 272
<u>Analysis</u>	Found: C, 44.98; H, 4.72; N, 7.30. C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Si calcd.: C, 48.98; H, 4.70; N, 8.16

NMR of intermediate:

$^1\text{H}$  0.83 (s, 3H, SiMe), 2.3 (s, 3H, CH<sub>3</sub>), 6.0 (s, 1H, CHSi), 6.5-7.5 (m, 6H, arom)  
 $^{13}\text{C}$  -5.6, 23.6, 60.1, 108.9, 117.3, 139.7, 156.3, 160.0  
 $^{29}\text{Si}$  -23.3

ii) Dichloromethylsilylmethyl bis(pyrid-2-one) (4.6b)

2-Trimethylsiloxypyridine 0.82 g

Dichloromethyl(methyldichlorosilane)silane 350  $\mu\text{l}$

Yield 1.04 g, 88%

M.P. 162-165°C

N.M.R.  $\delta/\text{ppm}$  (CD<sub>3</sub>OD, TMS)

$^1\text{H}$  0.56 (s, 3H, SiMe), 5.5 (s, 1H, CHSi), 6.8-9.0 (m, 8H, arom)  
 $^{13}\text{C}$  7.1, 65.5, 111.7, 116.6, 140.3, 146.1, 163.6  
 $^{29}\text{Si}$  -127.0

Mass m/z: 279/281 (M<sup>+</sup>-Cl, 3:1), 244

Analysis Found, C, 42.99; H, 4.47; N, 8.12.

C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>Si calcd.: C, 45.72; H, 3.84; N, 8.89

NMR  $\delta/\text{ppm}$  (DMSO-d<sub>6</sub>)

$^1\text{H}$  0.40 (s, 3H, SiMe), 0.57 (s, 3H, SiMe), 5.6 (s, 1H, CHSi), 5.8 (s, 1H, CHSi), 7.0-9.3 (m, 16H, arom)  
 $^{13}\text{C}$  5.5, 12.9, 62.6, 65.3, 114.9, 115.1, 115.5, 115.8, 137.1, 140.1, 146.9, 147.6, 161.5, 162.1,



$^{29}\text{Si}$  -128.9, -131.1

NMR of intermediate ( $\text{CDCl}_3$ )

$^1\text{H}$  0.50 (s, 3H, SiMe), 5.8 (s, 1H, CHSi), 6.7-8.4  
(m, 8H, arom)

$^{13}\text{C}$  -5.2, 55.0, 116.8, 118.6, 142.4, 148.4, 163.9

$^{29}\text{Si}$  -38.7

iii) Dichloromethylsilylmethyl bis(3-methoxypyrid-2-one) (4.6c)

2-Trimethylsiloxy-3-methoxypyridine 0.99 g

Dichloromethyl(methyldichloro)silane 350  $\mu\text{l}$

Yield 1.27 g, 90%

M.P. 180-183°C

N.M.R.  $\delta$ / ppm ( $\text{CD}_3\text{CN}+2$  drops  $\text{DMSO-d}_6$ , TMS)

$^1\text{H}$  0.50 (s, 3H, SiMe), 0.66 (s, 3H, MeSi), 3.9 (brs, 12H, OMe), 5.8 (s, 1H, CHSi), 6.0 (s, 1H, CHSi), 6.9-9.0  
(m, 12H, arom)

$^{13}\text{C}$  5.0, 13.6, 57.4, 57.6, 63.0, 66.9, 114.8, 122.6, 122.8,  
130.4, 130.8, 146.9, 147.2, 157.3, 157.6

$^{29}\text{Si}$  -128.5, -130.6

Analysis Found: C, 40.96; H, 4.17; N, 6.67.  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{Cl}_2\text{Si}$   
calcd.: C, 44.81; H, 4.30; N, 7.46

Synthesis of difluoromethylsilylmethylbis(6-methylpyrid-2-one) (4.8)

1.03 g (3 mmol) of hexacoordinated silyl chloride (4.6a) was suspended in 5 ml of dry benzene under nitrogen. 0.36 g (2 mmol) of antimony trifluoride was added to it and the reaction mixture was stirred for 3 hrs.. It was then diluted with excess water and extracted with chloroform (3x75 ml). The extract was dried over anhydrous magnesium sulphate and distilled under reduced pressure and dried under vacuum to yield a colourless solid.

M.P. 153-158°C

Yield 0.65 g, 84%

N.M.R.  $\delta$ / ppm ( $\text{CDCl}_3 + \text{CD}_3\text{CN}$ , 1:1, TMS)

$^1\text{H}$  2.6 (s, 6H, Me), 6.0 (s, 1H, CHSi), 6.3-7.6 (m, 6H, arom)

$^{13}\text{C}$  2.0 (t,  $^2J_{\text{CSiF}} = 20.7$  Hz, SiMe), 20.6, 21.4, 108.2, 112.3, 115.2, 118.3, 141.2, 142.8, 148.2, 149.5, 164.8, 165.0

$^{29}\text{Si}$  -82.9 (t,  $^1J_{\text{SiF}} = 262.7$  Hz)

Mass m/z 310 ( $\text{M}^+$ ), 295, 230

Analysis Found: C, 52.73; H, 5.21; N, 8.66.  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_2\text{Si}$   
calcd.: C, 54.18; H, 5.20; N, 9.03

***REFERENCES***

## REFERENCES

1. a) J.L.Gay-Lussac and L.J.Thenard, *Mem. Phys. Chem. Soc.*, Arceuil **2**, 317(1809)  
b) J.Davy, *Phil. Trans.*, **102**, 352(1812)
2. W.Dilthey, *Chem. Ber.*, **36**, 923(1903)
3. S.A.Sullivan, C.H.De Puy and R. Damrauer, *J. Am. Chem. Soc.*, **103**, 480(1981)
4. A.R.Bassindale and P G Taylor, In *The Chemistry of Organic Silicon Compounds*, Part 1, (Eds. S Patai and Z Rappoport), John Wiley, 1989.
5. R J.P.Corriu, C.Guerin and J.J.E Moreau, In *The Chemistry of Organic Silicon Compounds*, Part 1, (Eds. S Patai and Z Rappoport), John Wiley, 1989.
6. Robert R. Holmes, *Chem. Rev.*, **90**, 17(1990)
7. a) R.J.P.Corriu and C.Guerin, *Adv. in Organomet.Chem.*, **20**, 265(1982)  
b) R.J.P.Corriu, C.Guerin and J.J.E.Moreau, *Topics in Stereochemistry*, **15**, 43(1984)
8. J.Chojnowski, M.Cypryk and M.Michalski, *J. Organomet. Chem.*, **161**, C31(1978)
9. A.R.Bassindale, J.C.-Y.Lau and P.G.Taylor, *J. Organomet. Chem.*, **341**, 231(1988)
10. C.Eaborn and D.R.M.Walton, *J. Organomet. Chem.*, **4**, 217(1965)
11. L.H.Sommer, *Intra-Sci. Chem. Rep.*, **7**, 1(1973)

12. L.H.Sommer and W.D.Korte, *J. Am. Chem. Soc.*, **89**, 5802(1967)
- 13.. R.J.P.Corriu and C. Guerin, *J. Organomet. Chem.*, **198**, 231(1980)
14. J.H.Brewster, *J. Am. Chem. Soc.*, **81**, 5475(1959)
15. a) L.H.Sommer and J.McLick, *J. Am. Chem. Soc.*, **88**, 5359(1966)  
b) L.H.Sommer and J.McLick, *J. Am. Chem. Soc.*, **89**, 5806(1967)
16. R.J.P.Corriu, J.M.Fernandez and C.Guerin, *J. Organomet. Chem.*, **152**, 25(1978)
17. a) R.J.P.Corriu and G.Royo, *Bull. Soc. Chim. Fr.*, 1497(1972)  
b) R.J.P.Corriu and G.Royo, *Tetrahedron*, **27**, 4289(1972)
18. L.H.Sommer, W.D.Korte and P.G.Rodewald, *J. Am. Chem. Soc.*, **89**, 862(1967)
19. R.J.P.Corriu, G.Royo and A.De Saxce. *J. Chem. Soc., Chem. Commun.*, 892(1980)
20. C. Breliere, F.Carre, R.J.P.Corriu, A.De Saxce, M.Poirier and G.Royo, *J. Organomet. Chem.*, **205**, C1(1981)
21. C.Breliere, R.J.P.Corriu, and G.Royo, *J. Organomet. Chem.*, **107**, 148(1978)
22. C.Breliere, R.J.P.Corriu, A.De Saxce, F.Larcher and G.Royo, *J. Organomet. Chem.*, **164**, 19(1979)
23. C.Breliere, R.J.P.Corriu, and G.Royo, *J. Chem. Soc., Chem. Commun.*, 906(1976)

24. J.A.Dieters and R.R.Holmes, *J. Am. Chem. Soc.*, **109**, 1692(1987)
25. R.J.P.Corriu, and G.Royo, *J. Organomet. Chem.*, **40**, 229(1972)
26. R.J.P.Corriu, J.Masse, and G.Royo, *J. Chem. Soc., Chem. Commun.*, 252(1971)
27. R.J.P.Corriu, J.M.Fernandez and C.Guerin, *J. Organomet. Chem.*, **152**, 21(1978)
28. N.T.Anh and C.Minot, *J. Am. Chem. Soc.*, **102**,103(1980)
29. S.J.Berry, *J. Chem. Phy.*, **32**, 933(1960)
30. R.R.Holmes, R.O.Day, J.J.Harland, A.C.Sau and J.M.Holmes, *Organometallics*, **3**, 341(1984)
31. L.H.Sommer, J.McLick and C.M.Golino, *J. Am. Chem. Soc.*, **94**, 669(1972)
32. R.J.P.Corriu, and C.Guerin, *J. Organomet. Chem.*, **225**, 141(1982)
33. a) R.J.P.Corriu and J.Masse, *Tetrahedron Lett.*, 5197(1968)  
b) R.J.P.Corriu and J.Masse, *J. Organomet. Chem.*, **34**, 221(1972)
34. a) R.J.P.Corriu, C.Guerin and J.Masse, *J. Chem. Soc., Chem. Commun.*, 75(1975)  
b) R.J.P.Corriu, C.Guerin and J.Masse, *J. Chem. Res. Synop.*, 160(1977)
35. R.J.P.Corriu, J.M.Fernandez, C.Guerin and A.Kpton, *Bull. Soc. Chim. Belg.*, **89**, 783(1980)

36. a) R. Luckenbach, *Dynamics Stereochemistry of Pentacoordinated Phosphorus and Related Elements*, Thieme, Stuttgart, 1973.  
b) F.H.Westheimer, *Acc. Chem. Res.*, **1**, 70(1968)  
c) K.Mislow, *Acc. Chem. Res.*, **3**, 321(1970)  
d) P.Gillespie, P.Hoffman, H.Keusacek, D.Marquarding, S.Pfohl, F.Ramirez, E.A.Tsolis and I.Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687(1971)  
e) P.Gillespie, F.Ramirez, I.Ugi and D.Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91(1973)
37. R.R.Holmes, R.O.Day, J.J.Harland, A.C.Sau and J.M.Holmes, *Organometallics*, **3**, 341(1984)
38. R.R.Holmes, R.O.Day, J.J.Harland and J.M.Holmes, *Organometallics*, **3**, 347(1984)
39. A.R.Bassindale and T.Stout, *J. Chem. Soc., Chem. Commun.*, 1388(1984)
40. R.J.P.Corriu, A.Kpton, M.Poirier, G.Royo and J.Y.Corey, *J. Organomet. Chem.*, **277**, C25(1984)
41. R.J.P.Corriu, M.Poirier and G.Royo, *J. Organomet. Chem.*, **233**, 165(1982)
42. C.Breliere, F.Carre, R.J.P.Corriu, A.De Saxce, M.Poirier and G.Royo, *J. Organomet. Chem.*, **205**, C1(1981)
43. C.L.Frye, *J. Am. Chem. Soc.*, **92**, 1205(1970)
44. M.G.Voronkov, Yu.L.Frolow, V.M.D'Yakov, N.N.Chipanina, L.I.Gubanova, G.A.Gabrilova, L.V.Klyba and T.N.Aksamentova, *J. Organomet. Chem.*, **201**, 165(1980)

45. W.G.Farnham and R.L.Harlow, *J. Am. Chem. Soc.*, **103**, 4608(1981)
46. W.H.Stevenson and J.C.Martin, *J. Am. Chem. Soc.*, **104**, 309(1982)
47. F.Klanberg and E.L.Muetterties, *Inorg. Chem.*, **7**, 155(1968)
48. R.West, *J. Am Chem. Soc.*, **80**, 3246(1958)
49. J.J.Flynn and F.P.Boer, *J. Am. Chem. Soc.*, **91**, 5756(1969)
50. N.Serpone and K.A.Hersh, *J. Organomet. Chem.*, **84**, 177(1975)
51. A.Boudin, G.Creveau, C.Chuit, R.J.P.Corriu and C.Reye, *Angew. Chem., Int. Ed. Engl.*, **25**, 473(1986)
52. A.Boudin, G.Cerveau, C.Chuit, R.J.P.Corriu and C.Reye, *Angew. Chem., Int. Ed. Engl.*, **25**, 474(1986)
53. G.A.Olah and G.K.S.Prakash, *Chem. in Britain*, 916(1982)
54. G. Klebe and K.Hensen, *J. Chem. Soc., Dalton Trans.*, 5(1985)
55. R.Damrauer and S.E.Danahey, *Organometallics*, **5**, 1490(1986)
56. H.B.Burgi and J.D.Dunitz, *Acc. Chem. Res.*, **16**, 161(1983)
57. A.Kemme, J.Bleidelis, V.A.Pestunovich, V.P.Baryzhok and M.G.Voronkov, *Dokl. Akad. Nauk. SSSR*, **243**, 668(1978)
58. K.D.Onan, A.T.McPhail, C.H.Yoder and R.W.Hillyard Jr., *J. Chem. Soc., Chem. Commun.*, 209(1978)



59. C.H.Yoder, C.M.Ryan, G.F.Martin and P.S.Ho, *J. Organomet. Chem.*, **190**, 1(1980)
60. G.Klebe, J.W.Bats and K.Hensen, *J. Chem. Soc., Dalton Trans.*, 1(1985)
61. G.Klebe, J.W.Bats and K.Hensen, *Z. Naturforsch., B*, **38**, 825(1983)
62. C.Breliere, F.Carre, R.J.P.Corriu, M.Poirier and G.Royo, *Organometallics*, **5**, 388(1986)
63. J.A.Dieters and R.R.Holmes, *J. Am. Chem. Soc.*, **109**, 1686(1987)
64. J.A.Dieters and R.R.Holmes, *J. Am. Chem. Soc.*, **109**, 1692(1987); *J.Chem. Soc., Dalton Trans.*, 1131(1982)
65. H.-B.Burgi, *Angew Chem.*, **27**, 460(1975)
66. D.Britton and J.D.Dunitz, *J Am. Chem. Soc.*, **103**, 2971(1981)
67. M.J.Barrow, E.A.V.Ebsworth and M.M.Harding, *J.Chem. Soc., Dalton Trans.*, 1838(1980)
68. S.N.Tandura, M.G.Voronkov and N.W.Alekseev, *Top. Current Chem.*, **131**, 101(1986)
69. P.Hencsei and L.Parkanyi, *Reviews on Silicon, Germanium, Tin and Lead Compounds*, Ed. M.Gielen, Vrije Universiteit te Brussel, Vol. VIII, (1985).
70. A.A.Macharashvili, V.E.Shklover, Yu.T.Struchkov, G.I.Oleneva, E.P.Kramarova, A.G.Shipov and Yu.I.Baukov, *J. Chem. Soc., Chem. Commun.*, 683(1988)

71. R.Rudman, W.C.Hamilton, S.Novick and T.D.Goldfarb, *J. Am. Chem. Soc.*, **89**, 5157(1967)
72. M.J.Barrow, E.A.V.Ebsworth and M.M.Harding, *Acta Crystallogr., Sect. B*, **35**, 2093(1979)
73. M.J.Barrow and E.A.V.Ebsworth, *J. Chem. Soc., Dalton Trans.*, 563(1984)
74. A.B.Burg and E.S.Kuliajan, *J. Am. Chem. Soc.*, **72**, 3103(1950)
75. D.G.Anderson, A.J.Blake, S.Cradock, E.A.V.Ebsworth, D.W.H.Rankin and A.J.Welch, *Angew. Chem., Int. Ed. Engl.*, **25**, 1(1986)
76. I.R.Beattie and E.W.Parrett, *J. Chem. Soc.,(A)*, 1784(1966)
77. H.J.Campbell-Ferguson and E.A.V.Ebsworth, *J. Chem. Soc.,(A)*, 705(1967)
78. T.Stout, Ph.D. Thesis, The Open University, 1984
79. B.Marciniec and H.Gulinska, *J.Organomet. Chem.*, **146**, 1(1978)
80. S.Ya Khorshev, V.L.Tsvetkova and A.N.Egorochkin, *J. Organomet. Chem.*, **264**, 169(1984)
81. N.W.Alcock, V.M.Tracy and T.C.Waddington, *J. Chem. Soc., Dalton Trans.*, 2243(1976)
82. N.W.Alcock, V.M.Tracy and T.C.Waddington, *J. Chem. Soc., Dalton Trans.*, 2238(1976)
83. D.P.Gordon and B.A.Rana, *J. Organomet. Chem.*, **140**, 21(1977)

84. D.P.Gordon and B.A.Rana, *J. Organomet. Chem.*, **136**, 315(1977)
85. St N.Tandura, N.V.Alekseev and M.G.Voronkov, *Top. Curr. Chem.*, **131**, 99(1986)
86. J.J.Harland, J.S.Payne, R.O.Day and R.R.Holmes, *Inorg. Chem.*, **26**, 760(1987)
87. P.Arya, J.Boyer, R.J.P.Corriu, G.Lanneau and M.Perrot, *J. Organomet. Chem.*, **346**, C11(1988)
88. R.J.P.Corriu, G.Lanneau and M.Perrot, *Tetrahedron Lett.*, **29**, 1271(1988)
89. R.J.P.Corriu, C.Guerin, B.Henner and W.W.C.Wong Chi Man, *Organometallics*, **7**, 237(1988)
90. M.Kira, K.Sato and H.Sakurai, *Chem. Lett.*, 2243(1987)
91. M.Kira, K.Sato and H.Sakurai, *J. Org. Chem.*, **52**, 948(1987)
92. G.Cerveau, C.Chiut, R.J.P.Corriu and C.Reye, *J. Organomet. Chem.*, **328**, C17(1987)
93. A.Hosomi, S.Kohra, Y.Tominaga, *J. Chem. Soc., Chem. Commun.*, 1517(1987)
94. M.Kira, K.Sato and H.Sakurai, *J. Am. Chem. Soc.*, **110**, 4599(1988)
95. R.J.P.Corriu, C.Guerin and J.Moreau, *Top. Stereochem.*, **18**, 158(1984)
96. K.Tamao, J.Yoshida, H.Yamamoto, T.Kakui, H.Matsumoto, M.Takahashi, A.Kurita, M.Murata and M.Kumada, *Organometallics*, **1**, 355(1982)

97. J.I.Yoshida, K.Tamao, T.Kakui, A.Kurita, M.Murata, K.Yamada and M.Kumada, *Organometallics*, **1**, 369(1982)
98. K.Tamao, T.Kakui, M.Akita, T.Iwahara, R.Kanatani, J.Yoshida and M.Kumada, *Tetrahedron*, **39**, 983(1983)
99. R.Muller, *Z. Chem.*, **24**, 41(1984)
100. G.Cerveau, C.Chuit, R.J.P.Corriu and C.Reye, *Organometallics*, **7**, 786(1988)
101. A.Boudin, G.Cerveau, C.Chuit, R.J.P.Corriu and C.Reye, *Organometallics*, **7**, 1165(1988)
102. R.J.P.Corriu, *J. Organomet. Chem.*, **400**, 81(1990)
103. C. Breliere, R.J.P.Corriu, G.Royo, W.W.C.Wong Chi Man and J.Zwecker, *Organometallics*, **9**, 2633(1990)
104. R.J.P.Corriu, C.Guerin, J.Moreau, *Dynamic Stereochemistry at Silicon. In the Chemistry of Organic Silicon Compounds; Part 1* (Eds. S.Patai and Z.Rappoport), John Wiley 1989.
105. B.Becker, R.J.P.Corriu, C.Guerin, B.Henner, and Q.Wang, *J. Organomet. Chem.*, **359**, C33(1989)
106. B.Becker, R.J.P.Corriu, C.Guerin, B.Henner and Q.Wang, *J. Organomet. Chem.*, **369**, C25(1989)
107. J-L.Brefort, R.J.P.Corriu, C.Guerin, B.Henner and W.W.C.Wong Chi Man, *Organometallics*, **9**, 2080(1990)

108. A.Boudin, G.Cerveau, C.Chuit, R.J.P.Corriu and C.Reye, *J. Organomet. Chem.*, **362**, 265(1989)
109. C.L.Frye, G.E.Vogel and J.A.Hall, *J. Am. Chem. Soc.*, **83**, 996(1961)
110. M.G.Voronkov, V.M.Dyakov and S.V.Kirpichenko, *J. Organomet. Chem.*, **233**, 1(1982)
111. C.L.Frye, G.A.Vincent and G.L.Hauschildt, *J. Am. Chem. Soc.*, **88**, 2727(1966)
112. M.G.Voronkov, V.P.Baryshok, L.P.Petukhov, V.I.Rakhlin, R.G.Mirskov and V.A.Pestunovich, *J. Organomet. Chem.*, **358**, 39(1988)
113. V.A.Pestunovich, L.P.Petukhov, V.I.Rakhlin, B.Z.Shterenberg, R.G.Mirskov and M.G.Voronkov, *Dokl. Akad. Nauk SSSR*, **263**, 904(1982)
114. M.G.Voronkov, V.I.Rakhlin, L.P.Petukhov, R.G.Mirskov, B.Z.Shterenberg and V.A.Pestunovich, *Zh. Obshch. Khim.*, **54**, 2398(1984)
115. M.G.Voronkov, L.P.Petukhov, V.I.Rakhlin, B.Z.Shterenberg, R.G.Mirskov, S.N.Adamovich and V.A.Pestunovich, *Zh. Obshch. Khim.*, **56**, 964(1986)
116. M.G.Voronkov, V.A.Pestunovich, L.P.Petukhov and V.I.Rakhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 699(1983)
117. G.Cerveau, C.Chuit, R.J.P.Corriu, N.K.Nayyar and C.Reye, *J. Organomet. Chem.*, **389**, 159(1990)
118. M.T.Attar-Bashi, C.Eaborn, J.Vencl and D.R.M.Walton, *J. Organomet. Chem.*, **117**, C87(1976)

119. J.Boyer, C.Brelier, R.J.P.Corriu, A.Kpoton, M.Poirier and G.Royo, *J. Organomet. Chem.*, **311**, C39(1986)
120. M.Kira, K.Sato and H.Sakurai, *J. Am. Chem. Soc.*, **110**, 4599(1988)
121. T.J.Batterham, *NMR Spectra of Simple Heterocycles*, Wiley-Interscience, 1973.
122. R.J.P.Corriu, G.Dabosi and M.Martineau, *J. Organomet. Chem.*, **186**, 25(1984)
123. S.K.Chaudhury and O.Hernandez, *Tetrahedron Lett.*, 99(1979)
124. A.R.Bassindale, and T.Stout, *J. Organomet.Chem.*, **238**, C41(1982)
125. H.K.Chu, M.D.Johnson and C.L.Frye, *J. Organomet. Chem.*, **271**, 327(1984)
126. D.Kummer, S.C.Chaudhury, J.Seifert, B.Deppisch and G.Mattern, *J. Organomet. Chem.*, **382**, 345(1990)
127. G.Klebe, J.W.Bats and H.Fuess, *J. Am. Chem. Soc.*, **106**, 5902(1984)
128. M.S.Gordon, personal communication.
129. A.A.Macharashvili, V.E.Shklover, Yu.T.Struchkov. M.G.Voronkov, B.A.Gostevsky, I.D.Kalikhman, O.B.Bannikova, V.A.Pestunovich, *J. Organomet. Chem.*, **340**, 23(1988); **356**, 23(1988)
130. R.R.Holmes, R.O.Day, V.Chandrasekhar and J.M.Holmes, *Inorg. Chem.*, **24**, 2009(1985); **24**, 2016(1985)
131. F.P.Boer, J.J.Flynn and J.W.Turley, *J. Am. Chem. Soc.*, **90**, 6973(1963)

132. J.J.Harland, R.O.Day, J.F.Vollano, A.C.Sau and R.R.Holmes, *J. Am. Chem. Soc.*, **103**, 5269(1981)
133. R.J.P.Corriu, G.Lanneau, M.Perrot, *Tetrahedron Lett.*, **28**, 3941(1987)
134. P.Arya, J.Boyer, F.Carre, R.J.P.Corriu, G.F.Lanneau, M.Perrot, C.Priou, *Angew Chem., Int. Ed. Engl.*, **28**, 1016(1988)
135. B.Becker, R.J.P.Corriu, C.Guerin, and B.J.L.Henner, *J. Organomet. Chem.*, **369**, 147(1989)
136. J.Boyer, R.J.P.Corriu, R.Perz, and C.Reye, *Tetrahedron*, **37**, 2165(1981)
137. J.Boyer, R.J.P.Corriu, R.Perz, and C.Reye, *Synthesis*, 558(1981)
138. R.J.P.Corriu, R.Perz, and C.Reye, *Tetrahedron*, **39**, 999(1983)
139. M.Fujita, and T.Hiyama, *J. Am. Chem. Soc.*, **106**, 4629(1984)
140. S.Kohra, Y.Hayashida, Y.Tominaga, A.Hosomi, *J. Che. Soc., Chem. Commun.*, 1411(1986)
141. S.Kohra, Y.Hayashida, and Y.Tominaga, *Tetrahedron Lett.*, **29**, 89(1988)
142. A.Hosomi, A.Shirahata, and H.Sakurai, *Tetrahedron Lett.*, **33**, 3043(1978)
143. G.Majetich, A.M.Casares, D.Chapman, and M.Behuke, *J. Org. Chem.*, **51**, 1745(1986)
144. M.Kira, M.Kobayashi, and H.Sakurai, *Tetrahedron Lett.*, **35**, 4081(1987)
145. B.Becker, R.J.P.Corriu, and C.Guerin, *J. Organomet. Chem.*, **369**, C33(1989)

146. J.Kowalski and Z. Lasocki, *J. Organomet. Chem.*, **116**, 75(1976)
147. R.J.Pugmire, D.M.Grant, L.B.Townsend, and R.K.Robins, *J. Am. Chem. Soc.*, **95**, 2791(1973)
148. G.B.Barlin, and T.J.Batterham, *J. Chem. Soc.,(B)*, 516(1967)
149. J.Lau, Ph.D.Thesis, Open University, Milton Keynes, 1986.
150. J.A.Dieters, R.R.Holmes, *Abstract of a presentation at the 197th National Meeting of the American Chemical Society*, Dallas, TX, April 1989, INOR 423.
151. R.J.P.Corriu, and M.J.Henner, *J. Organomet. Chem.*, **74**, 1(1974)
152. R.J.P.Corriu, and J.C.Young, *Hypervalent Silicon Compounds*. In *The Chemistry of Organic Silicon Compounds*, Eds. S.Patai, Z.Rappoport, Wiley, N.Y. 1989.
153. J.Boyer, R.J.P.Corriu, R.Perz, and C.Reye, *Tetrahedron*, **39**, 117(1983)
154. R.J.P.Corriu, and R.Perz, *tetrahedron Lett.*, **26**, 1311(1985)
155. I.Kuwajima, and E.Nakamura, *J. Am. Chem. Soc.*, **97**, 3257(1975)
156. I.Kuwajima, E.Nakamura, *J. Am. Chem. Soc.*, **99**, 1265(1977)
157. R.J.P.Corriu, V.Huynh, J.J.E.Moreau, and M.Pataud-Sat, *Tetrahedron Lett.*, **23**, 3257(1982)
158. E.Nakamura, T.Murofushi, M.Shimizu, and I.Kuwajima, *J. Am. Chem. Soc.*, **98**, 2346(1976)



159. I. Kuwajima, E.Nakamura, and K.Hashimoto, *Tetrahedron*, **39**, 975(1983)
160. J.J.Berzelius, *Ann. Chim. Phy.*, **27**, 291(1824)
161. M.Kumada, K.Tamao, and J.J.Yoshida, *J. Organomet. Chem.*, **239**, 115(1982)
162. C.L.Frye, *J. Am. Chem. Soc.*, **86**, 3170(1964)
163. R.Muller, and L.Heinrich, *Chem. Ber.*, **94**, 1943(1961)
164. A.Rosenheim, B.Raibmann, and G.Schendel, *Z. Anorg. All. Chem.*, **196**, 60(1931)
165. E.Leukevics, O.Pudova, and R.Sturkovich, *Molecular Structure of Organosilicon Compounds*, Ellis Horwood, Chichester, 1989.
166. D.Kummer, K.E.Gaisser, and T.Seshadri, *Chem. Ber.*, **110**, 1950(1977)
167. D.Kummer, and T.Seshhadri, *Chem. Ber.*, **110**, 2355(1977)
168. D.Kummer, K.E.Gaisser, J.Serferth, and R.Z.Wagner, *Z. Anorg. All. Chem.*, **459**, 145(1979)
169. D.Kummer, and T.Seshadri, *Z. Anorg. All. Chem.*, **432**, 147(1977)
170. C.Brelier, F.Carre, R.J.P.Corriu, and G.Royo, *Organometallics*, **7**, 1006(1988)
171. M.J.Buchanan, R.H.Cragg, and A.Steltner, *J. Organomet. Chem.*, **120**, 189(1976)
172. R.W.Hillyard Jr, C.M.Ryan, and C.H.Yoder, *J. Organomet. Chem.*, **153**, 369(1978)